1 **Contribution of amide-based coagulant polyacrylamide as precursors of**
2 **haloacetamides and other disinfection by-products**

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Abstract

Coagulation is a widespread method of drinking water treatment. Coagulation can mitigate the formation of disinfection by-products (DBPs) through removing their precursors. Here we report that the amide-based organic polymer coagulants polyacrylamide (PAM) and its monomer acrylamide (AM) can serve as a source of HAcAm and other DBPs including trihalomethanes (THMs) and haloacetonitriles (HANs) during chlor(am)ination. The impact of the key experimental parameters, including reaction time, Cl_2 or NH_2Cl dose, pH and initial bromide concentration on the formation of DBPs was investigated. Furthermore, the major reaction pathways for AM transformation and DBP formation during chlor(am)ination are proposed and include *N*-chlorination, addition, and substitution. Jar tests demonstrated that coagulation by alum coupled with PAM achieved greatest removal of DOC and UV_{254} , compared with alum and PAM alone. Treatment with PAM didn't significantly promote the formation of THMs and HANs during post-chlorination, indicating that the PAM residual hardly contributes to THM and HAN formation. However, coagulation by applying alum salt and PAM increased total HAcAm concentrations by 2.2-3.1 $\mu\text{g/L}$ at the higher PAM dose (2.0 mg/L), compared with alum alone. Therefore, the contribution of PAM to the formation of HAcAm cannot be ignored. The results highlight that the generation of secondary pollutants from the amide-based engineered organic polymer coagulants in drinking water should be considered; that is, they can adversely affect water quality because of their ability to enhance DBPs generated during downstream disinfection. Accordingly, the understanding of the stability and reactivity of PAM in the presence of disinfectants could help to better evaluate their contribution to the formation of HAcAms, THMs, and HANs, which has important implications for their environmental fate, transport, and responsible applications.

Keywords

Polyacrylamide; coagulant; haloacetamide; disinfection by-products; drinking water.

1. Introduction

Most countries now have water quality regulations or guidelines that require drinking water treatment plants (DWTPs) to ensure that finished water has acceptable levels of pathogens, toxins and contaminants [1]. Disinfectants (chlorine and chloramines) are still commonly added in DWTPs to inactivate pathogens and inhibit their occurrence in distribution and storage [2, 3]. However, chlorine and chloramines, two widely used low-cost disinfectants, can react with dissolved organic and inorganic matter in water to form disinfection by-products (DBPs) of potential human health concern [4]. The US Environmental Protection Agency (USEPA) promulgated the Stage 2 Disinfectants and Disinfection By-products Rule, which set the maximum contaminant level to 80 µg/L for four trihalomethanes (THMs) and 60 µg/L for five haloacetic acids (HAAs) to reduce the potential adverse effects associated with DBPs [5]. Emerging and unregulated nitrogenous DBPs (N-DBPs), particularly haloacetonitriles (HANs), halonitromethanes (HNMs), haloacetamides (HAcAms), *N*-nitrosamines (NAs), and aromatic halogenated DBPs, have lower mass concentrations in drinking water compared to the regulated carbonaceous DBPs (C-DBPs), including THMs and HAAs [6]. Nevertheless, they are attracting increasing concern because of their high toxicities [7-11]. One study indicated that HAcAms and HANs are the first and second-most cytotoxic groups of 50 DBPs based on the determination of the effective concentration, i.e. 50% inhibition of bioluminescence (Microtox) or cell density (*E. coli* assays) [12].

Although DWTPs are exploiting new technologies to remove natural organic matter (NOM) and different types of dissolved and undissolved emerging anthropogenic contaminants during drinking water treatment, coagulation/flocculation remains the most commonly used method to remove dissolved matter, particles and colloids that can impart colour to a water source, create turbidity, or retain bacterial and viral organisms [13]. In particular, this is because of its cost effectiveness and ease of operation [14]. Commonly used coagulants are classified into two categories: inorganic coagulants and organic polymeric coagulants. Organic polymer coagulants have remarkable abilities to coagulate even at low doses, produce smaller sludge volumes without reducing alkalinity and reducing costs by up to 25–30% (relative to inorganic coagulants) [15]. Polyacrylamide (PAM) and its derivatives are extensively used as coagulants because ultra-high molecular weight polymers can be prepared easily from its monomer acrylamide (AM) [16].

When using PAM, there is a high probability that it and its monomer AM will partly pass through conventional treatment processes and undergo further reactive transformation during subsequent chlor(am)ination. Further, where chlorine and/or chloramines are used as pre-oxidants, the residual disinfectants can also react with the coagulants (e.g., PAM) during coagulation. Most previous studies exploring DBPs precursors have focused on NOM and anthropogenic contaminants [17-19]. A series of studies investigated the impact of common coagulants on the removal of precursors to DBPs during drinking water treatment [20-22]. These studies found that enhanced coagulation can remove NOM and anthropogenic contaminants, which are regarded as precursors of DBPs, thus mitigating the formation of DBPs during subsequent chlorination. However, several studies have indicated that some coagulant aids (PAM and poly(diallyldimethylammonium chloride)) could increase the formation of THMs or NAs [21, 22]. Moreover, one of these studies even indicated that PAM can serve as the precursor of *N*-Nitrosodimethylamine with the formation potential of 8.0 ng/mg [22]. However, little is known about whether PAM and AM can serve as halogenated C- and N-DBP precursors during disinfection. Following application of PAM, the formation of halogenated C-DBPs and N-DBPs during downstream chlorination or chloramination is a potential risk. Accordingly, the stability and reactivity of PAM in the presence of disinfectants may help to better predict their contribution to the formation of DBPs and guide responsible application. To our knowledge, this study is the first to investigate the contribution of PAM to the formation of halogenated N-DBPs. Therefore, the objectives were to investigate to what extent amide-based coagulants act as precursors of HA₂Am and other halogenated DBPs during drinking water treatment, and to elucidate their transformation mechanisms by identifying their intermediate products.

2. Materials and methods

2.1. Materials

Water samples were collected from the Huangpu River (HP) and a local secondary wastewater treatment plant (QY) and were stored in the dark at 4 °C until used. The aim of the selection of wastewater effluent was to investigate the effects of different water quality on the experiment results according to that the wastewater effluent, when discharged into natural waters, can also

serve as the source water of drinking water. The characteristics of the waters are summarized in [Table S1](#). AM (99%), nonionic PAM (molar weight = $2\text{--}14 \times 10^6$ Da), aluminum sulfate octadecahydrate ($\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$), aquatic humic acids (HA) and methyl-*tert*-butyl ether (MTBE) were purchased from Aladdin Industrial Inc. (Shanghai, China). To facilitate direct comparison of molar DBP yields from AM and PAM, the repeating unit of PAM (i.e. $\text{C}_3\text{H}_5\text{ON} = 71$ Da) was used when calculating molar mass. Thus, a $50 \mu\text{M}$ solution of AM and PAM contained the same mass of monomer/polymer, even though their respective molecular weights are in reality different ([Fig. S1](#)). The characteristics and sources of DBP standard are available in [Table S2](#). A free chlorine (Cl_2) stock solution was prepared from a sodium hypochlorite solution (active chlorine > 5%). Preformed monochloramine (NH_2Cl) stock solutions were prepared daily by dissolving ammonium chloride in ultrapure water adjusted to pH 8.0 with sodium hydroxide and chilled to 4°C . Sodium hypochlorite was then slowly added to the rapidly stirred solution with a hypochlorite to ammonia molar ratio of at least 1:1.2 [17]. All other chemical reagents were at least analytical grade and obtained from Sinopharm Chemical Reagent Co., Ltd (Shanghai, China) unless otherwise noted. All solutions were prepared in ultrapure water produced by a Millipore Milli-Q Gradient water purification system ($18 \text{ M}\Omega \cdot \text{cm}$, Billerica, USA).

2.2. Experimental procedures

Chlor(am)ination experiments. Batch experiments were conducted in 100 mL headspace-free screw-cap amber glass vials with polytetrafluoroethylene-lined septa in the dark at $25.0 \pm 0.5^\circ\text{C}$. Predetermined volumes of Cl_2 or NH_2Cl and each coagulant stock solution were injected into 10 mM phosphate or carbonate buffer to obtain the desired initial concentrations. After predetermined time intervals, 10 mL portions of the aqueous solution were withdrawn and immediately extracted by liquid–liquid extraction to analyse the HAcAm concentration to avoid the interference of the quenching agent on the formation of HAcAms [23]. And another 40 mL portion of the aqueous solution was withdrawn and quenched with ascorbic acid at the initial molar concentration of the Cl_2 or NH_2Cl to analyse the other DBPs.

Coagulation experiments. Each source water was treated using aluminum sulfate octadecahydrate (alum salt, 10 mg/L as Al) alone, PAM alone, and alum salt together with a low or high PAM dose

(i.e., 0.5 mg/L or 2.0 mg/L). Coagulation experiments was conducted in a jar test apparatus (ZR4-6, Zhongrun Water Industry Technology Development Co., Ltd, Shenzhen, China). Coagulant was added to the raw water, before being mixed rapidly at 250 rpm for 1.5 min, stirred slowly at 50 rpm for 15 min, and then settled for 30 min, which is common practice among Chinese DWTPs [24]. A supernatant sample from 2 cm below the surface was collected and filtered through 0.22 μm membrane to detect the water quality characteristics, and then 10 mg/L free chlorine, which can provide the desired 24 h chlorine residual of $1 \pm 0.5 \text{ mg-Cl}_2/\text{L}$, was added to investigate the formation of HAcAm and other DBPs. The error bars in all figures represent the relative standard deviation of the three replicates.

2.3. Analytical methods

Cl_2 and NH_2Cl concentrations were measured using a portable photometer (HACH Pocket ColorimeterTMII, Loveland, USA) with an *N,N*-diethyl-1,4-phenylenediamine sulfate (DPD)-free chlorine reagent and DPD total chlorine reagent (HACH, Loveland, USA), respectively. Dissolved organic carbon (DOC) and total dissolved nitrogen (TDN) were measured by a TOC analyzer equipped with a TNM total nitrogen detection unit (TOC-VCPH, Shimadzu Corporation, Japan). Dissolved organic nitrogen (DON) was the difference between TDN and dissolved inorganic nitrogen (ammonia, nitrate, and nitrite). Ammonia, nitrate, and nitrite were measured with a UV-vis spectrophotometer (HACH DR6000, Loveland, USA). The turbidity was measured by a turbidimeter (HACH 2100P, Loveland, USA). Bromide was measured by an ion chromatography (Dionex ICS-1000, USA). Detailed procedures for the analysis of the DBPs and intermediate products are available in the elsewhere and supporting information (Text S1 and Table S3) [25]. DBPs yields are defined in % mol/mol as the molar ratio of the produced DBPs to the initial PAM/AM concentration (eq 1).

$$\text{DBP yield} = \frac{\text{Molar concentration of formed DBPs}}{\text{Initial PAM repeating unit or AM molar concentration}} \times 100\% \quad (1)$$

To investigate the role of bromide on the formation and speciation of DBPs, the bromine

substitution factor (BSF) for the main species, THMs, HANs, and HAcAms (i.e. THMs, dihaloacetonitriles (DHANs), and dihaloacetamides (DHAcAms)), were calculated [26]. The BSF is defined as the ratio of the molar concentration of bromine incorporated into a given class of DBP relative to the total molar concentration of chlorine and bromine in that class, respectively. To compare the BSF in an unbiased way between different DBP classes, we further divided the BSF values by the number of halogen atoms (three in THMs and two in DHANs or DHAcAms). BSF values for THMs, DHANs, and DHAcAms were calculated using the following formulas (eqs 2-4).

$$\text{BSF (DHAcAms)} = \frac{[\text{BCAcAm}] + 2[\text{DBAcAm}]}{2[\text{DHAcAms}]} \quad (2)$$

$$\text{BSF (THMs)} = \frac{[\text{BDCM}] + 2[\text{DBCM}] + 3[\text{TBM}]}{3[\text{THMs}]} \quad (3)$$

$$\text{BSF (DHANs)} = \frac{[\text{BCAN}] + 2[\text{DBAN}]}{2[\text{DHANs}]} \quad (4)$$

3. Results and discussion

3.1. Formation of HAcAms during the chlor(am)ination of AM and PAM

[\[Figure 1\]](#)

[Fig. 1](#) indicated that PAM and AM, an organic polymer coagulant and its monomer, both act as precursors of HAcAms. To focus on the HAcAm, the pH of the aqueous solution was buffered at 6.0 unless otherwise noted, which resulted in higher yields of HAcAms. The formation of dichloroacetamide (DCAcAm) and trichloroacetamide (TCAcAm) were slow within the first 6 h, subsequently gradually increasing with time ([Fig. 1a](#) and [Fig. 1b](#)). The maximum yield of DCAcAm was from the chloramination of PAM at 48 h, eventually reaching $0.64 \pm 0.04\%$. DCAcAm yields from AM were first higher than from PAM, but the reverse applied with longer

chlorination times, implying that the α -carbon group in AM was di-halogenated by Cl_2 more rapidly than that in PAM. In contrast, DCACAm was generated from AM more slowly than from PAM during chloramination. In general, chlorination produced more DCACAm and TCACAm from PAM compared with chloramination in the absence of bromide, while the reverse results were observed for AM. The yields of DCACAm and TCACAm showed the same trend, that is, a continuous increase with increasing Cl_2 or NH_2Cl doses up to 1 mM (Fig. 1c and Fig. 1d). TCACAm was undetectable (limit of detection = 0.05 $\mu\text{g/L}$) until the Cl_2 or NH_2Cl dose increased to 0.25 mM, which is consistent with previous studies reporting that an increasing Cl_2 dose favoured the formation of TCACAm than DCACAm [27, 28]. Fig. 1e and Fig. 1f showed the DCACAm and TCACAm yields after the 24 h chlor(am)ination of AM and PAM at different pHs. As expected, the yields of DCACAm and TCACAm decreased with increasing pH from 5 to 9. This pattern can be explained by the increased hydrolysis and chlorination of DCACAm and TCACAm at higher pH values [23]. The decrease in DCACAm yields were proportionally lower than those in TCACAm with increasing pH. The concentrations of TCACAm from the chlorination of PAM and chloramination of AM at pH 8 were both below the limit of detection (0.05 $\mu\text{g/L}$), and TCACAm was undetectable at pH 9. This result is attributed to the increasing hydrolysis and chlorination of HACams with increasing pH and number of halogens [29]. Comparing the DHACAm yields in Fig. 1 and Fig. S2, the presence of bromide promoted the formation of total DHACAm. This phenomenon can be explained by bromine acting as a more efficient halogenation agent than chlorine. Concerning the BSF values (Fig. 1g and Fig. 1h), DHACams presented a first increasing and then decreasing trend, which is consistent with the previously reported variation of the BSF for DHACams during the chlorination and chloramination of water from Taihu Lake with different added bromide concentrations [30]. This was explained by reactions involving bromochloroamines and bromamines formed during chloramination in the presence of bromide being more important in the formation of HACams than those involving HOBr in the presence of chlorine [30]. Similarly, another study found that the median BSF value for DHACAm in 146 chloraminated drinking water supply system samples was dramatically higher than in 395 chlorinated drinking water supply system samples [31]. The decrease of BSF for DHACAm was attributed to the increasing bromide promoting the formation of brominated trihaloacetamides and

other brominated by-products, which act as bromine sinks, at higher initial bromide concentrations [32].

3.2. Formation of THMs and HANs during the chlor(am)ination of AM and PAM

[Figure 2]

As shown in Fig. 2, the formation of THMs and HANs during the chlor(am)ination of AM and PAM at various reaction conditions were conducted. The results showed that the both chloroform (CF) and dichloroacetonitrile (DCAN) yields increased with increasing reaction time up to 48 h. The yields of CF during the chlorination of AM and PAM were both lower than during chloramination, except for the 48 h data, which does not agree with the results of previous studies. Generally, chlorination favours the formation of CF compared to chloramination because Cl_2 is more oxidising than NH_2Cl [33]. Previous studies have shown that the reaction of NH_2Cl with the amide group is insignificant, and it has been proposed that Cl_2 first reacts with amide to form an *N*-haloamide, followed by enolization and subsequent halogenation at the α -carbon group during the chlorination of AM and PAM [23, 34]. The data indicate that *N*-chlorination by Cl_2 consumed more active Cl_2 than NH_2Cl in the initial reaction period because of its stronger oxidising ability (Table S4). Therefore, chloramination produced more CF than chlorination during the initial reaction period (< 24 h). Once the *N*-chlorination reaction had completed, halogenation at the α -carbon led to the formation of CF. The chlorination of AM/PAM produced higher CF yields than chloramination at 48 h, typified by respective yields of $0.4 \pm 0.03\%$ / $0.4 \pm 0.03\%$ and $0.3 \pm 0.02\%$ / $0.4 \pm 0.03\%$. It has also been shown that the CF yields from PAM are higher than AM under the same disinfection conditions, which results from the low reactivity Cl_2 of with unsaturated bonds [35]. The yields of DCAN during the chlorination of AM and PAM were $0.02 \pm 0.001\%$ and $0.02 \pm 0.001\%$ after 48 h reaction time, respectively. AM generated more DCAN than PAM during chloramination, while DCAN yields from AM during chlorination were, at first, higher than those from PAM but this pattern reversed over longer contact times. This behaviour can be attributed to the simultaneous formation and degradation of DCAN, which is linked to its low

stability in the presence of Cl_2 [36]. Trichloroacetonitrile was undetectable (limit of detection = $0.1 \mu\text{g/L}$) under selected disinfection conditions. Fig. S3 shows the kinetic profiles of TCNM formation. TCNM yields continuously increased, reaching $0.04 \pm 0.003\%$ after 48 h. Meanwhile, chlorination favours the formation of TCNM compared to chloramination.

CF and DCAN yields both increased with increasing Cl_2 or NH_2Cl dose. The maximum CF yields during the chloramination of AM and PAM reached $0.4 \pm 0.03\%$ and $0.6 \pm 0.04\%$, respectively, at highest chlorine dose (i.e. Cl_2 or NH_2Cl dose = 1.0 mM). Meanwhile, PAM generated higher CF yields than from AM at a range of Cl_2 or NH_2Cl doses. The CF yields from chlor(am)ination of AM and PAM both exhibited a gradually increasing trend as pH increased from 5 to 9 (Fig. 2e and Fig. 2f), which is consistent with previous studies highlighting the important of base-catalysed reactions to CF formation during the chlor(am)ination of natural water [37]. While the chlorination of AM/PAM formed CF at pH 5, CF was undetectable during chloramination at the same pH. Hypochlorous acid, which is major chlorine species at pH 5, plays a significant role in CF formation during the chlorination of AM and PAM [38]. In contrast, chloramination produced more CF than chlorination from AM/PAM at higher pH values (i.e. 6, 7, 8, and 9). The maxima CF yields from the chlorination of AM and PAM at pH 9 were $0.9 \pm 0.07\%$ and $1.4 \pm 0.09\%$. The effect of pH on the formation of DCAN was quite different to that of CF. As expected, acidic conditions favoured the formation of DCAN. This pattern can be explained by the increased hydrolysis and chlorination of DCAN at higher pH values [36]. Notably, the highest DCAN yields occurred at pH 6 during chlorination [27].

Comparing Fig. 2g and Fig. 2h, the aggregate THM yields (i.e. the sum of CF, bromodichloromethane (BDCM), dibromochloromethane (DBCM), and bromoform (BF)) and DHAN yields (i.e. the sum of DCAN, bromochloroacetonitrile (BCAN), and dibromoacetonitrile (DBAN)) from AM and PAM both increased with increasing bromide concentration during chlorination. The THM yields increased with increasing bromide concentration during the chloramination of AM and PAM (Fig. S4). Moreover, the BSF for THMs also continuously increased, which indicates that increasing bromide concentration promoted the incorporation of bromine into the THMs. Unlike THMs, the DHAN yields did not continuously increase with increasing bromide concentration (Fig. S4). It was probably attributed that the lower formation of

DHAN results in the detection error and the formation of other brominated by-products [32]. Concerning the BSF values, DHANs and DHAcAms presented the same tendency; that is, a first increasing and then decreasing trend. In addition, bromine was incorporated more easily into the DHANs than the DHAcAms because DHANs had a higher BSF than the DHAcAms, although the BSFs are lower than those of the THMs.

3.3. Proposed formation pathway for THMs, HANs, and HAcAms

[Figure 3]

AM (500 μ M) was chlor(am)inated at pH 6 to investigate its decomposition mechanism and to identify the intermediate products that could lead to the formation of N-DBPs. Several peaks were observed in the total ion chromatogram recorded by GC/MS, such as P105 (retention time (RT) = 4.28 min), P123 (RT = 12.6 min), and P175 (RT = 15.4 min). Molecular formulas and structures of these compounds are proposed based on the proposed mass obtained from the NIST 14 database and fragmentation patterns observed in EI mode.

As shown in Fig. 3, the formation pathways of DBPs from the reactions of Cl_2 or NH_2Cl and AM were proposed (the PAM formation pathway is not shown in the figure). Cl_2 or NH_2Cl addition reactions form P123 or its isomer during the chlor(am)ination of AM via an initial Cl^+ transfer to the double bonds to give a chloronium ion, which is followed by the addition of OH^- [39]. P123 or its isomer were also detected by GC/MS (Fig. S5). A fragment ion from P123 with m/z 88 shows a molecular weight decrease of 35 from that of P123, which is assigned to the loss of $-\text{Cl}$ during electron impact. The successive halogenation of the carbon α to the carbonyl by Cl_2 or NH_2Cl produced CF via the base-catalysed haloform reaction. Moreover, the Cl_2 or NH_2Cl addition reactions followed by the halogen substituted reaction on the σ -carbon or the successive replacement of the hydrogen on the β -carbon result in the formation of P175. For chlorinated compounds, the isotopic abundance ratio of 3:1 for $^{35}\text{Cl} : ^{37}\text{Cl}$ provides a characteristic pattern [40]. For example, an isotopic abundance ratio of 9:6:1 with m/z 126/128/130 and m/z 140/142/144 of the fragment ion in P175 (Fig. S6) suggests that this fragment ion contained two chlorine atoms.

A fragment ion from P175 with m/z 140/142/144 shows a molecular weight decrease of 35 from that of P175, which is assigned to the loss of -Cl during electron impact. Therefore, we proposed P175 was 1,2,2-trichloro-propionamide or 1,1,2-trichloro-propionamide. P175 is oxidised subsequently by Cl_2 or NH_2Cl to form HAcAms.

Yu and Reckhow recently showed that the *N*-chlorination reaction occurs rapidly during the chlorination or chloramination of molecules that contain amide groups because the hydrogen atoms of the acetamide groups are easily substituted by halogen atoms [23]. The molecular ion cluster of P105 (Fig. S7) with m/z ratio of 105/107 indicated the presence of one chlorine atom. The EI mass spectrum of P105 showed two dominant ion clusters (m/z 105/107 and 70), the mass difference of 35 Da corresponds to the loss of -Cl. Based on the above, P105 is proposed to be *N*-chloro-acrylamide. P105 (i.e. *N*-chloro-acrylamide) can form vinylamine via the Hofmann reaction [41]. The vinylamine are chlorinated at α -amine group by Cl_2 or NH_2Cl to form monochlorinated amines or dichlorinated amines, followed by the Cl_2 or NH_2Cl addition reactions on unsaturated bonds [38]. Halogenation, elimination and hydrolysis lead to the formation of THMs, HANs and HAcAms [42].

3.4. Contribution of PAM as the precursor of HAcAms and other DBPs

[Figure 4]

Fig. S8 showed the removal of DOC and UV_{254} in source waters after different coagulation treatment. For all waters, the alum salt alone (10.0 mg/L as Al) treatment produced higher DOC removal than PAM alone (at 0.5 mg/L and 2.0 mg/L). This indicates that nonionic PAM is ineffective for the removal of anionic NOM [15]. The changes of bromide after coagulation can be neglected because bromide removal by drinking water coagulants is insignificant [43, 44]. When the alum salt and PAM were added simultaneously during coagulation, DOC removal increased by 6–13% or 23–36% to 50–63% compared to alum salt or PAM (0.5 mg/L) alone. The decrease in UV_{254} were proportionally higher than those in DOC, indicating that the aromatic DOM components were removed preferably. Fig. S9 presents turbidity removal in source waters with

different coagulation methods. For all waters, turbidity removal was most effective with alum salt and 2.0 mg/L PAM. Depending on the source water type and polymer dose, the percent removal of turbidity in the alum-PAM coagulated waters was 40–98% higher than for the alum controls. However, turbidity removal by PAM alone slightly lower than that of alum alone.

The three raw waters produced 8.1 ± 0.5 , 14.0 ± 0.7 , and 5.1 ± 0.4 $\mu\text{g/L}$ total HAcAm (DCAcAm, TCACAm, bromochloroacetamide (BCAcAm), and dibromoacetonitrile (DBAcAm)), in Fig. 4). Brominated HAcAms were not detected during the chlorination of HA water due to the low bromide concentration. Precursor removal by coagulation with alum alone led to total HAcAm reductions of between 41.8% and 61.4% to 3.7 ± 0.3 , 5.5 ± 0.4 , and 3.0 ± 0.3 $\mu\text{g/L}$ in the three treated waters of HP, QY, and HA. Coagulation of three waters (HP, QY, and HA) with PAM alone increased total HAcAm concentrations by 70-76% to 6.4 ± 0.5 , 9.1 ± 0.7 , and 5.1 ± 0.4 $\mu\text{g/L}$ at the lower PAM dose (0.5 mg/L) compared with alum alone coagulation. Coagulation of three waters (HP, QY, and HA) with PAM alone at the higher dose (2.0 mg/L) increased total HAcAm concentrations by 137–149% to 9.0 ± 0.5 , 13.4 ± 0.8 , and 7.1 ± 0.4 $\mu\text{g/L}$ compared with alum alone coagulation. HP and HA samples, treated by coagulation under the same conditions (PAM alone), even produced more total HAcAms (9.0 ± 0.6 and 7.1 ± 0.4 $\mu\text{g/L}$) than that (8.0 ± 0.6 and 5.1 ± 0.3 $\mu\text{g/L}$) for the corresponding raw waters, due to the higher PAM residual. These results indicate that only a small fraction of existing HAcAm precursors for HAcAm were removed by PAM coagulation, while simultaneously the PAM residual added new HAcAm precursors. Therefore, the trade-off between the formation and mitigation of total HAcAm depends on the added PAM dose and water quality characteristics. Coagulation of three waters by the addition of alum salt and PAM, as coagulant and coagulant aids respectively, were also investigated. Results showed that alum-PAM coagulation substantially enhanced the removal of both DOC and UV_{254} compared with the results for alum or PAM alone. The total HAcAm concentration after alum-PAM coagulation of HP and HA waters increased to 4.5 ± 0.4 and 3.4 ± 0.2 $\mu\text{g/L}$ at the lower PAM dose compared to alum alone (3.6 ± 0.2 and 3.0 ± 0.2 $\mu\text{g/L}$), while the total HAcAms concentration after alum-PAM coagulation of QY water decreased. This can be explained by the effluent organic matter in QY water accounting for the majority of HAcAm formation. Coagulation by applying 10 mg/L alum salt + 2 mg/L PAM increased total HAcAm concentrations by 45-75% to 6.7 ± 0.5 , 7.7 ± 0.5 ,

and 5.2 ± 0.4 $\mu\text{g/L}$ at high PAM dose (2.0 mg/L) compared with alum alone. It should be noted that coagulation HA sample with 0.5 mg/L PAM + 10 mg/L $\text{Al}_2(\text{SO}_4)_3$ not produced TCACAm. This phenomenon can be explained by that coagulation with 0.5 mg/L PAM + 10 mg/L $\text{Al}_2(\text{SO}_4)_3$ enhance the removal of TCACAm precursor compared to coagulation with $\text{Al}_2(\text{SO}_4)_3$ alone and the residual PAM was relatively lower compared to coagulation with 2.0 mg/L PAM + 10 mg/L $\text{Al}_2(\text{SO}_4)_3$. The TCACAm yield was far lower than DCACAm and CF from PAM and NOM. Taken together, TCACAm was undetected in the 0.5 mg/L PAM + 10 mg/L $\text{Al}_2(\text{SO}_4)_3$ sample. These data indicate the relative contributions of PAM and NOM to HACAm formation were comparable during the competitive reaction of chlorine with NOM and PAM, considering that a mass of NOM in raw water can be removed by coagulation treatment and the alum-PAM coagulation may enhance the removal of NOM compared to alum alone.

[Fig. S10](#) and [Fig. S11](#) presented the formation of THMs and HANs following coagulation. It is obvious that the formation of THMs and HANs were controlled by coagulation of raw waters by 29-85% and 25-78%, respectively. DOC and UV_{254} are collective parameters and also correlated with the THM formation potential in drinking water samples. [Fig. S8](#) indicates the aromatic DOM components (UV_{254}) were removed preferably, which led to the high removal of THM precursors. Aromatic DOM represents the major source of THM precursors [18]. Therefore, although the residual PAM can introduce new THM precursors, removal of existing precursors by alum-PAM coagulation was more significant. As for HANs, chlorination of PAM produced less HANs than HACams or THMs ([Fig. 1](#) and [Fig. 2](#)). Moreover, there was a substantial decrease in HANs formed from the chlorination of raw waters and alum coagulated waters ($> 50\%$), whereas coagulation with alum-PAM slightly enhanced the concentration of HANs in one sample (HP water) compared to that coagulation with alum alone ($< 10\%$). Taken together, the PAM residual hardly contributed to overall HAN formation.

4. Conclusions

This study is to report that amide-based organic polymer coagulants and their monomers (i.e. PAM and AM) can adversely affect water quality, beyond the direct exposure to AM and PAM dissolved in water, because of their ability to produce toxic DBPs during disinfection. The maximum yields

for CF, DCAN, DCaAm, and TCaAm during chlor(am)ination of PAM in this study were $1.7 \pm 0.1\%$, $0.05 \pm 0.003\%$, $0.8 \pm 0.05\%$, and $0.2 \pm 0.008\%$, respectively. Jar tests indicated that the PAM residual in water after coagulation can serve as the precursor for HAcAms and other DBPs. Although DOC and UV₂₅₄, by alum-PAM were more effective than for the alum salt alone, it increased total HAcAm concentrations by 3.1, 2.3, and 2.2 µg/L at the higher PAM dose (2.0 mg/L).

We emphasise that the potential for DBP formation from several organic polymer coagulants and related derivatives should not be overlooked. PAM and its monomer AM have the same magnitude of molar yields of HAcAms with those formed from typical amino acids and antibiotics, and PAM loadings reaches ppm levels during coagulation in DWTPs, which has the chance to react with disinfectants (chlorine/chloramines) during pre-chlor(am)ination and/or post-chlor(am)ination. Thus, the outcome of this work helps to define better the risk posed by amide-based coagulants upon their reaction with disinfectants, which in turn should help to inform the responsible development of amide-based coagulants for use in water and wastewater treatment and monitoring.

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Appendix A. Supplementary data

Supplementary data related to this article is available in this appendix.

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Figure captions

Fig. 1. Effect of reaction time (a and b), Cl_2 or NH_2Cl dose (c and d), pH (e and f), and bromide concentration (g and h) on the formation and speciation of HAcAms during the chlor(am)ination of AM and PAM. (Conditions: initial AM or PAM conc. = 0.05 mM, reaction time = 24 h, Cl_2 or NH_2Cl dose = 0.25 mM, pH = 6.0 ± 0.2 , and bromide = 0, unless otherwise noted).

Fig. 2. Effect of reaction time (a and b), Cl_2 or NH_2Cl dose (c and d), pH (e and f), and bromide concentration (g and h) on the formation and speciation of THMs and HANs during the chlor(am)ination of AM and PAM. (Conditions: initial AM or PAM conc. = 0.05 mM, reaction time = 24 h, Cl_2 or NH_2Cl dose = 0.25 mM, pH = 6.0 ± 0.2 , and bromide = 0, unless otherwise noted).

Fig. 3. Proposed formation pathway for THMs, HANs, and HAcAms during the chlor(am)ination of AM.

Fig. 4. HAcAm formation during the chlorination of HP (a), QY (b), and HA (c) water following coagulation, sedimentation and filtration with the addition of different coagulants.

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