Contribution and Removal of Watershed and Cationic Polymer *N*-Nitrosodimethylamine Precursors

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N-nitrosodimethylamine (NDMA) is a disinfection by-product formed when chloramines react with precursors derived from watersheds or water treatment polymers. The authors examined the sorption potential of both precursor groups to powdered and granular activated carbon (PAC and GAC). Activated carbon reduced the formation potential (FP) of NDMA by 30 to 80% when only watershed precursors were present. Polydiallyldimethylammonium chloride (polyDADMAC) precursors were not removed well by activated carbon. Seven samples of polyDADMAC from across the United States produced 47 ± 3 ng NDMAFP/mg active polymer after coagulation and settling, which is about one-third of the NDMAFP formed in ultrapure (> 18.2 MΩ-cm) water. Polyamine (340 ng/mg) formed NDMA when diluted in ultrapure water with chloramines, but the precursors were effectively removed by activated carbon. PolyDADMAC use always increased the NDMAFP of the settled water, regardless of dose; this suggests that the optimum dose should be based on turbidity removal with consideration for balancing NDMA formation.

Keywords: *disinfection by-product, granular activated carbon,* N-*nitrosodimethylamine, polyDADMAC, powdered activated carbon*

Disinfection with aqueous chlorine produces regulated trihalomethanes (THMs) and haloacetic acids (HAAs) when bulk natural organic matter (NOM) is present in the source water. Alternative disinfectants such as chloramines have been shown to reduce the formation of chlorinated disinfection by-products (DBPs) in drinking water (Guay et al, 2005). As a result, between 2007 and 2010, the number of US water utilities using chloramines rose from 944 to 1,298—a 37% increase (Li, 2011). Unfortunately, chloramination can produce *N*-nitrosodimethylamine (NDMA) through reactions with organic nitrogen sources (Richardson et al, 2007; Mitch et al, 2003). Decades of research have addressed mitigation of THM and HAA formation, but less is known about NDMA mitigation strategies. Strategies to limit NDMA formation involve physical removal or oxidation of organic precursors (Krasner et al, 2013). This article focuses on physical removal strategies and evaluates these strategies using the two major classes of precursors that appear to exist: watershed-derived precursors and in-plant sources such as cationic polymers.

BACKGROUND

NDMA is a drinking water DBP with a carcinogenic risk level of 10^{-6} at lifetime exposure levels of 0.7 ng/L (USEPA, 2002). The US Environmental Protection Agency (USEPA) is considering regulating NDMA in the United States, as indicated by NDMA's inclusion in Unregulated Contaminant Monitoring Rule 2 (UCMR 2, 2007). Canada and two US states (California and Massachusetts) have already begun regulating NDMA in the form of notification or guidance at levels of 10–40 ng/L (CDPH, 2013; Health Canada, 2011; Massachusetts Office of EEA, 2004). Given that USEPA is expected to make a regulatory determination in 2015, finding strategies to mitigate NDMA formation during drinking water treatment is essential.

NDMA precursors are thought to be associated with anthropogenic sources containing reactive organic nitrogen groups such as secondary and tertiary amines (Krasner et al, 2013). Among several other sources (such as agricultural chemicals and rubbers used in distribution system gaskets), the primary factors affecting NDMA formation in drinking waters are thought to be cationic polymer use and trace organic compounds (pharmaceuticals, personal care products) in wastewater-affected surface waters (Krasner et al, 2013; Selbes et al, 2013; Shen & Andrews, 2011a, 2011b; Teefy et al, 2011; Park et al, 2009; Kohut & Andrews, 2003; Wilczak et al, 2003). The most important NDMA mitigation strategies are thought to be precursor preoxidation, alternative polymers, activated carbon (AC), and optimization of polymer use (Krasner et al, 2013). AC has been shown to be an effective mitigation strategy for NDMA precursors of wastewater

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origin (Hanigan et al, 2012). Powdered AC (PAC) and granular AC (GAC) removed NDMA precursors better than dissolved organic carbon (DOC) or organic matter absorbing ultraviolet light at 254 nm (UV_{254}), which are good indicators of THM and HAA precursors. Other research has also demonstrated removal of wastewater NDMA precursors with AC (Farré et al, 2011; Sacher et al, 2008). To date, the authors are not aware of any research that examines removal of polymer-derived precursors by AC and the effects on NDMA formation. Furthermore, it is unknown whether the removal of watershed-derived precursors by AC could potentially be offset by polymer use in terms of NDMA formation.

Study objective. The objective of the current study was to understand the contribution of watershed and polymer-derived precursors to NDMA formation and the ability to control that contribution using PAC and GAC. Eq 1 was developed to represent the conceptual differences in reactivity and treatability of watershed and polymer NDMA precursors:

$$\begin{aligned} \mathrm{NDMAFP_{total}} = {} & (1 - \Sigma_1^i \eta_{\mathrm{WS}})\ \mathrm{NDMAFP_{WS}} \\ & + (1 - \Sigma_1^i \eta_{\mathrm{pDMC}})\ \mathrm{NDMAFP_{pDMC}} \\ & + (1 - \Sigma_1^i \eta_{\mathrm{pAMN}})\ \mathrm{NDMAFP_{pAMN}} \end{aligned} \tag{1}$$

in which NDMAFP is the NDMA formation potential and η is the dose-dependent percent removal of precursors by AC, oxidation, or other processes for different classes of NDMAFP precursors, including watershed-derived precursors ($_{\mathrm{WS}}$), polydiallyldimethylammonium chloride (polyDADMAC)–derived precursors ($_{\mathrm{pDMC}}$), and polyamine-derived precursors ($_{\mathrm{pAMN}}$). One goal of the current research was to determine estimates of the parameters in Eq 1.

The authors also set out to investigate factors controlling the sorption of precursors such as PAC contact time, initial precursor concentration, and point of PAC addition in the treatment train. Bench-scale experiments were used to validate pilot-scale observations about decreases in NDMAFP attributable to sorption and increases in FP from polymer addition.

MATERIALS AND METHODS

Sampling sources and experiments. ***Bench scale.*** Treated secondary wastewater effluent and surface water were taken from local sources (Phoenix, Ariz.) and transported directly to a laboratory where they were stored at 4°C until use (less than two weeks). Wastewater was sampled from an activated sludge treatment plant (secondary effluent), and surface water was sampled from the Central Arizona Project (CAP) canal system that receives Colorado River water. All samples were stored and transported in either amber borosilicate bottles or high-density polyethylene containers. Typical water quality parameters are shown in Table 1.

For these samples, the bituminous-based PAC WPH®[1] was used; this selection was based on previous results that showed this PAC provided stronger adsorption of watershed-derived precursors than a lignite PAC (Hanigan et al, 2012). Hydrated aluminum sulfate was obtained onsite from a local water treatment plant. The polyDADMAC used in most of the testing was Clarifloc® C-4410,[2] obtained onsite as a 20% active polymer solution. In one experiment, multiple polyDADMAC samples were compared; each of these—Clarifloc C-308P,[2] C-338,[2] C-358,[2] C-378,[2] and C-4410, as well as SW-104[3]—was individually obtained from other treatment plants. Polyamine was obtained onsite from a full-scale treatment plant as a mix of 20% polymer and 80% aluminum chlorohydrate (CC 2220[4]). Bench-scale filtration was completed using 0.6-µm glass fiber filters[5] that had been precombusted at 500°C for 5 h.

Experiments were conducted using a six-paddle gang stirrer[6] with 2-L rectangular vessels. For experiments with a coagulant and polymer, the coagulant was added to a 1.5-L surface water (25°C) sample approximately 30 s before the polymer. PAC was hydrated in reagent water for > 24 h before use at a concentration of 10 g/L. The polymer and the coagulant were added into the most turbulent zone located beneath the water surface and directly above the paddle. Samples were rapidly mixed at 100 rpm for 2 min, followed by flocculation for 20 min at 30 rpm, and settling for 1 h (0 rpm). In some cases, the supernatant was decanted (750 mL), PAC was added to the supernatant, and the sample was mixed for 1 h at 100 rpm. The samples were then filtered.

For experiments without coagulants, PAC was added directly to samples and mixed at 100 rpm. Unless specified, the PAC contact time was 1 h. Samples were filtered after PAC contact. In blended samples, wastewater and surface water were mixed before addition of PAC to simulate source waters impacted to varying degrees by wastewater.

A bench-scale GAC column was packed with Norit® GAC 820.[7] The column was 2.5 cm in diameter and 12 cm in length and was loaded at a rate of 176 m/d. The column had a short empty bed contact time (EBCT) of 1 min, but the experiment was

TABLE 1 Typical raw water quality parameters for selected source waters

Source Water	DOC *mg/L C*	SUVA *L/mg-m*	TDN *mg/L as N*	NDMAFP *ng/L*	Ammonia *mg/L as N*	pH	Turbidity *ntu*
WW (secondary effluent)	5.3–5.5	1.9	3.4	250–1,000	< 0.2	~ 7.7	NM
SW	4.0	1.8	0.02	13	< 0.2	~ 8.1	2–10
10% WW + 90% SW	4.2	1.8	1.2	105	< 0.2	NM	NM
Ohio River water	3–4	NM	1.3	9–19	< 0.2	7.6–7.8	22–41

DOC—dissolved organic carbon, NDMAFP—*N*-nitrosodimethylamine formation potential, NM—not measured, SUVA—specific ultraviolet absorbance, SW—surface water, TDN—total dissolved nitrogen, WW—wastewater not conducted to investigate sorption but rather a potential interaction between the GAC surface and polyDADMAC.

Pilot scale. A pilot plant was operated in December 2012, treating water from the Ohio River in Louisville, Ky. Two treatment trains were operated in parallel to compare treatment scenarios. The treatment trains included presedimentation, coagulation/flocculation, sedimentation, and filtration (Figure 1). Filters contained either anthracite or GAC. The GAC (F820[1]) was installed in January 2007 (about half of which was replaced in July 2010) and was effectively DOC-saturated (< 17% removal). The anthracite (100 cm anthracite, 25 cm sand, 176 m/d) and GAC (EBCT = 8.3 min, 100 cm GAC, 25 cm sand, 176 m/d) filters were backwashed approximately every 48 h of runtime. In some experimental scenarios, Norit PAC 20BF[7] (selected for onsite availability) was added ahead of the presedimentation basins—the hydraulic retention time (HRT) was 30–60 min, based on experimental scenario—or in the coagulation basin with the polyDADMAC. The pilot plant used C-308P polyDADMAC polymer. Pilot testing was completed over two weeks, during which changes occurred in influent turbidity (range of 22–42 ntu). After changes to the operation of the pilot plant were made, steady state was achieved before samples were taken; approximately three residence times (2.5 h) passed between sample collections.

Two experimental scenarios were conducted during each 24-h period; samples from the previous afternoon/evening setup were taken in the morning, the operational conditions were changed, samples were taken again in the afternoon, and operational conditions were changed again for sampling the following morning. Grab samples taken nearly simultaneously (did not follow a plug of water) because the plant was assumed to be at equilibrium with only slow changes in influent FP. The pilot plant was operated using the same coagulant (ferric chloride) dose as in the parallel full-scale plant where jar tests were conducted to determine optimal turbidity removal and polyDADMAC and PAC doses could be varied. Pilot-scale experiments were conducted using water at ambient temperature (9.4–10.6°C), and samples were collected in duplicate and stored in an onsite refrigerator until they were transported overnight to the laboratory refrigerator in coolers containing ice packs.

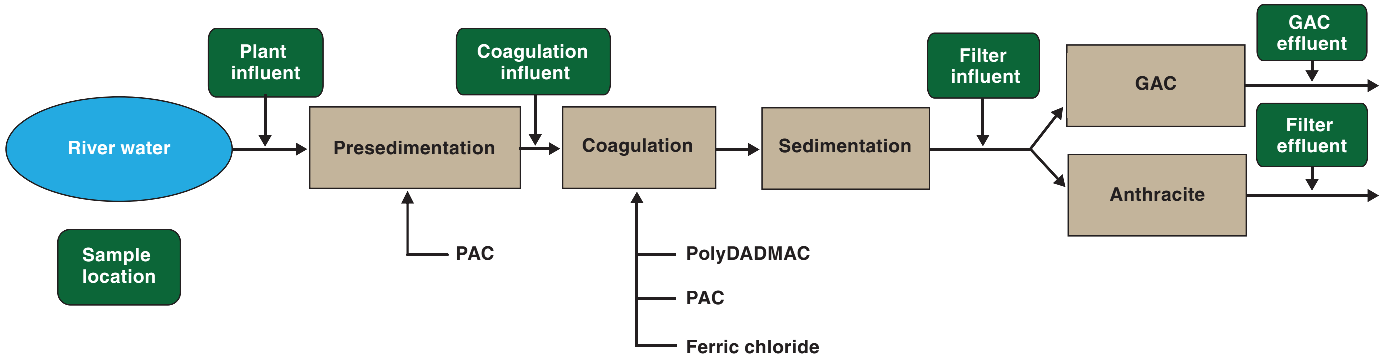
Full scale. Three full-scale treatment plants with GAC were sampled, two of which were designed for total organic carbon (TOC) removal (THM precursor removal; extended EBCT). Two plants were treating surface water from the central United States; one of these plants used Clarifloc C-4410 and GAC at an EBCT of 21 min, and the other used Clarion A410P[8] and GAC at an EBCT of 3.8 min. The third plant was treating local surface water using Clarifloc C-358 and GAC at an EBCT of 20 min. All three treatment plants used the same GAC, F400.[1]

No chlorine was added upstream of the GAC for the two plants with the high EBCTs, whereas chloramines were added upstream of the GAC for the plant with the low EBCT. NDMAFP was measured across the GAC contactor, and no chlorine was added upstream. The GAC contactors used for TOC removal had varying times of loading since regeneration (300–19,000 bed volumes). In one sampling, the plant with the low EBCT had GAC that had been in service for two months (one filter sampled) or 15 months (the other filter sampled). However, both filters were spent in terms of TOC removal (15% removal).

Reagents. All reagent water was > 18.2 MΩ-cm purified water.[9] Sodium hypochlorite (NaOCl, 5.65–6%), sodium tetraborate, boric acid, and ascorbic acid were purchased from a supplier,[10] and ammonium chloride was obtained from another source.[11] Table 2 provides the typical virgin carbon characteristics for AC used in this study; not all carbon used was virgin.

Chloramination. For NDMAFP experiments, DOC and ammonia were first measured in the samples. Ammonia was negligible in all samples (< 0.2 mg/L as N). Samples were chloraminated using a preformed monochloramine (NH_2Cl) solution. Bench-scale samples were chloraminated at 3 × mg/L of DOC = mg/L of NH_2Cl as Cl_2, and pilot-scale samples were mixed with 18 mg/L NH_2Cl as Cl_2. To prepare the NH_2Cl solution, NaOCl was diluted with borate buffer (pH 8) and ultrapure (> 18.2 MΩ-cm) water to a final concentration of 1.7–2.2 g/L as Cl_2. The NaOCl solution was added slowly to a pH 8 borate-buffered ammonium

FIGURE 1 Schematic of one of the two pilot-plant treatment trains



Source: Krasner et al, forthcoming

GAC—granular activated carbon, PAC—powdered activated carbon, polyDADMAC—polydiallyldimethylammonium chloride

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TABLE 2 Activated carbon characteristics

Activated Carbon	Experiment	Type	Iodine Number *mg/g*	pH_{zpc} (Reference)
F400*	Three full-scale plants	GAC	1,000	8.5 (Dastgheib et al, 2004)
F820*	Pilot scale	GAC	900	6.1 (Huang et al, 2004)
Norit®† 820	Bench scale	GAC	970	10 (this study)
Norit 20BF	Pilot scale	PAC	800	Not available
WPH®*	Bench scale	PAC	800	5.9 (Siddiqui et al, 1994)

GAC—granular activated carbon, PAC—powdered activated carbon, pH_{zpc}—pH at the point of zero charge

*Calgon Carbon, Pittsburgh, Pa.
†Cabot Norit Americas, Marshall, Texas

Characteristics are for virgin activated carbon and thus likely do not represent used carbons.
All carbons had a base material of bituminous coal.

chloride solution. The final NH_2Cl stock solution contained 200 m*M* borate and had an N-to-Cl_2 molar ratio of 1.2. The NH_2Cl concentration was measured after a reaction period of 1 h at 25°C using an indophenol reagent[12] to produce a colorimetric response that was measured using a spectrophotometer.[13]

Samples were buffered at pH 8 using 2 m*M* borate and dosed with NH_2Cl. Samples were chloraminated and allowed to react in the dark for 72 h at 25°C, after which 5 m*M* ascorbic acid was added to quench any remaining NH_2Cl.

Analytical methods. NDMA was quantified in a process similar to method 521 (USEPA, 2004) employing addition of an isotopically labeled internal standard, solid-phase extraction onto AC cartridges and quantification using gas chromatography/mass spectrometry (GC/MS) in positive chemical ionization mode, with ammonia as the reagent gas. A complete description of the GC/MS conditions and NDMA analytical methods is available elsewhere (Hanigan et al, 2012).

DOC and total dissolved nitrogen were measured using a TOC analyzer (with an attached total nitrogen measurement [TNM] unit)[14] by applying Method 5310 B (*Standard Methods,* 2005). UV absorbance was measured using both the UV-visible spectrophotometer[13] and a UV-visible photodiode array spectrophotometer.[15] The pH at the point of zero charge (pH_{zpc}) was measured in a manner similar to that used by Dastgheib and colleagues (2004) in which 200 mg GAC is added to 40 mL of preboiled 0.1-*M* sodium chloride solutions having different pH values and agitated for 48 h. The solution at which the pH does not change over 48 h is considered the pH_{zpc}.

Statistical analysis. Statistical analysis was conducted using the analysis of variance and Tukey's honestly significant difference (Tukey's HSD) functions inside the R environment (R Core Team, 2013). Initial rejection of the null hypothesis resulted in pairwise difference of means analysis. For post hoc analysis, the confidence level was set at 0.95.

RESULTS

Removal of watershed-derived precursors by PAC. Multiple operating scenarios (22 discrete scenarios, 88 samples) at the pilot plant were intended to test the hypothesis that watershed-derived precursors are removed well by PAC, whereas polyDADMAC-derived precursors are not. Raw water NDMAFP varied between 9 and 21 ng/L during pilot testing. When PAC was added to the presedimentation basins without cationic polymer, 3 to 20 mg/L of PAC reduced the NDMAFP by 4 to 17 ng/L (reduction = 57% ± 14%), respectively, when compared with the raw water. Increasing the PAC dose led to greater NDMAFP reduction. PAC removed more NDMAFP (46–82%) than DOC (removal = 10% ± 7%) or UV_{254} (removal = 7% ± 5%). This was similar to previous bench-scale findings (Hanigan et al, 2012) in which between 37 and 91% of precursors of wastewater origin were amenable to removal by PAC (3 to 75 mg/L of WPH or Norit Hydrodarco B[7]). These experiments confirmed that PAC effectively removes watershed-derived precursors at the pilot scale.

NDMAFP was not linearly reduced as a function of PAC dose or contact time; reduction varied daily based on influent water quality. For example, 7 mg/L PAC reduced NDMAFP between 43 and 72% across five days of sampling, with the greatest reduction occurring at the shortest contact time (influent NDMAFP = 17 ng/L in both cases); 20 mg/L PAC reduced NDMAFP between 52 and 82% across four days of sampling (influent NDMAFP = 14 and 21 ng/L, respectively). Thus, some NDMA precursors may be more amenable to removal by PAC than others, and influent precursor sources and background organic matter varied with time in the source water. During the pilot-plant study, river flow varied from 3,600 to 8,430 m^3/s, and presumably, the wastewater impact was less when river flow was greater. During the pilot testing, influent turbidity varied from 22 to 42 ntu, and pH varied from 7.6 to 7.8.

Varying the contact time in the pilot-scale presedimentation basin between 30 and 60 min at PAC doses of 7 and 20 mg/L produced similar NDMAFP reductions. Further investigation of the effects of PAC contact time was completed at bench scale using 90% surface water and 10% wastewater (Figure 2). Contact time with PAC varied over typical HRTs for PAC treatment (15 to 120 min), and PAC dose ranged from 3 to 20 mg/L. All PAC doses decreased NDMAFP relative to the control sample, but little to no change in removal of precursors occurred after 15 min of contact time. Reduction by PAC in absolute NDMAFP at the pilot plant (4–17 ng/L NDMAFP) was less than that at bench scale (28–45 ng/L NDMAFP). However, the source waters were

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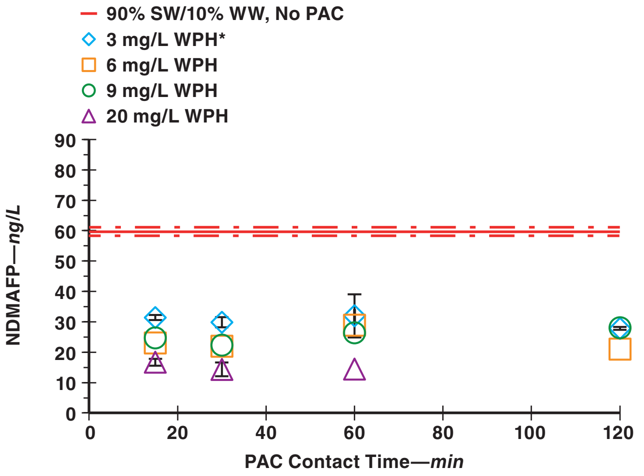
different, the initial precursor loading was higher at bench scale (surface water mixed with wastewater), and NDMAFP percent removals were similar (standard deviation of percent removal always less than 6% at PAC doses of 3, 6, 9, and 20 mg/L during contact times of 0.25, 0.5, 1, and 2 h). Results from the pilot plant and the bench-scale experiments demonstrated that precursor adsorption is rapid enough to be achievable in water treatment plants under reasonable conditions.

To further investigate competitive sorption of NDMA precursors with NOM, blended water was produced by mixing wastewater and surface water with the intent of varying both DOC and NDMA precursor loading. Blends between 10% wastewater/90% surface water and 100% wastewater resulted in initial DOC concentrations between 3.9 and 5.3 mg/L, respectively. Initial UV_{254} varied from 5.1 to 10 m^{-1}. A single PAC dose (3 mg/L) was applied to all surface water/wastewater blends. DOC removal was 5% with low wastewater content and generally decreased as the percentage of wastewater in the blend increased. UV_{254} removal exhibited a similar generally decreasing trend (from 14 to 9% with increasing wastewater content). NDMAFP of the blended waters increased with higher percent wastewater; 10% wastewater/90% surface water had an NDMAFP of 52 ng/L, compared with 132 ng/L for the 50% wastewater/50% surface water blend and 162 ng/L for 100% wastewater. Removal of NDMA precursors with 3 mg/L PAC varied from 15 to 40 ng/L with increasing wastewater content (Figure 3). When normalized to the NDMAFP of the associated control sample (the NDMAFP after PAC treatment was normalized to the NDMAFP of the control sample for a specific WW/SW blend), NDMAFP removal was 17% to 34% at this relatively low PAC dose of 3 mg/L. Percent precursor removal was independent of initial NDMAFP or percent wastewater, as would be expected for trace organic contaminant removal in the presence of competing NOM (Westerhoff et al, 2005; Knappe et al, 1998). In other words, the same percent precursor removal was observed independent of a higher (more wastewater) or lower (less wastewater) NDMAFP precursor level (Figure 3).

Removal of watershed-derived precursors by GAC. Pilot tests were conducted to assess the removal of watershed-derived and polymer-derived precursors by GAC versus an anthracite filter in filter adsorbers that had been operated for years (since 2007). DOC removal across the GAC filter was only 0.4 mg/L C (17%), indicating that the filter was nearly exhausted for DOC removal, whereas the anthracite removed only ~ 4% of DOC. In this test, the settled water had somewhat more NDMAFP than the raw water (26 versus 19 ng/L), the cause of which is unknown and could be precursor released from the pilot plant itself (e.g., rubbers, piping). When no polymer was used upstream during coagulation/settling, GAC reduced NDMAFP from 26 to 18 ng/L, whereas no change was seen across the anthracite filter. Even very close to complete DOC breakthrough, GAC contactors removed some of the precursors (in this case, 31% with an EBCT of 8.3 min); however, it is not clear how much of the precursor material was watershed-derived. In previous research (Hanigan et al, 2012), when a similar GAC was used with an EBCT of 10 min, at 83% DOC breakthrough, NDMAFP reduction was still ~ 85%. Influent precursor loading was higher in the previous study

FIGURE 2 PAC reduction of NDMA formation at multiple contact times

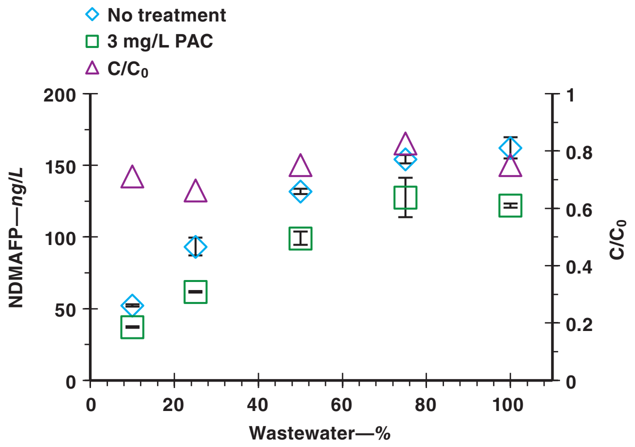


DWTP—drinking water treatment plant, NDMA—*N*-nitrosodimethylamine, NDMAFP—NDMA formation potential, PAC—powdered activated carbon, SW—surface water, WW—wastewater

*Calgon Carbon, Pittsburgh, Pa.

PAC was contacted at 100 rpm in a gang stirrer. Blended source water (90% SW/10% WW) was intended to simulate a wastewater-impacted DWTP influent. Error bars show individual samples (duplicate samples) with markers displaying the average.

FIGURE 3 PAC adsorption of precursors at varying initial precursor loadings



NDMAFP—*N*-nitrosodimethylamine formation potential, PAC—powdered activated carbon

Precursor loading was adjusted by blending different amounts of surface water and wastewater at ambient pH. PAC contact time = 2 h. Triangles represent the fraction of NDMAFP remaining (C/C_0) after PAC treatment (right axis). Error bars show individual samples (duplicate samples) with markers displaying the average.

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(116 versus 26 ng/L NDMAFP). In the current study, the pilot plant was set up to use GAC for biodegradation rather than adsorption, whereas the previous study (Hanigan et al, 2012) used virgin GAC at bench scale. Moreover, only one set of tests was available to evaluate GAC with no PAC or polymer.

Contribution of polymers to NDMAFP in the presence of watershed-derived precursors. Nine polymers at varying doses were tested in different source waters to determine the contribution of polymer addition to NDMAFP in addition to watershed-derived precursors. As part of an ongoing project, the polymers were acquired from onsite dosing tanks during routine sampling by several utilities from across the United States. At the pilot plant, three polymer doses—0.1, 0.4, and 1 mg/L polyDADMAC (dose of the active ingredient/polymer)—were used to simulate low-, typical-, and overdosed polymer conditions, respectively. Before polymer addition, raw water at the pilot plant contained 9 to 19 ng/L NDMAFP. Addition of polyDADMAC solution during coagulation increased NDMAFP between 1 and 57 ng/L across the coagulation basin, depending on polymer dose. Equivalent yield is 62 ng NDMAFP/mg polyDADMAC (active polymer) (three polyDADMAC concentrations, linear fit, $R^2 = 0.99$). If the polymer is assumed as monomeric, it is found to have a somewhat low yield (0.01%) compared with other known NDMA precursors—e.g., dimethylamine = 1.2–2.6% (Selbes et al, 2013; Mitch & Sedlak, 2004). The increase in NDMAFP across the coagulation basin at all polymer doses indicates that not all polymer-associated precursors are removed during the coagulation and settling process.

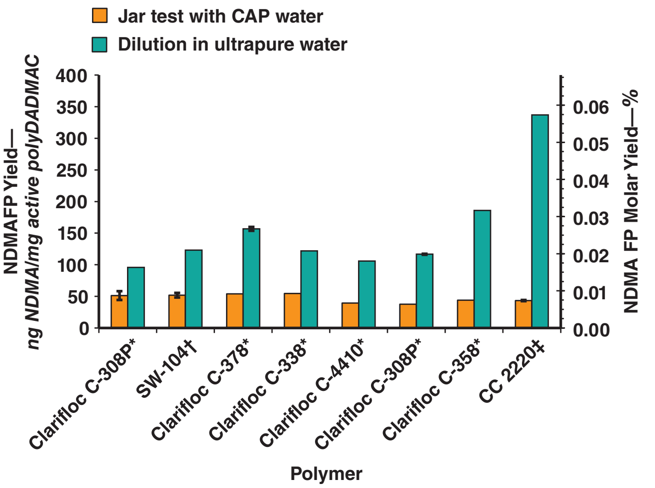
Separate bench-scale testing (jar tests using a surface water source) used an array of polymer doses up to high, unrealistic doses, e.g., 0.1 to 25 mg/L polyDADMAC (active polymer), added simultaneously with alum. Although polymer doses greater than 2 mg/L active polymer are typically not practiced at full scale, they were intentionally used here to confirm the contribution of polymer to settled water NDMA formation.

Results indicated that in either Ohio River water or CAP water, a dose of 1 mg of polyDADMAC resulted in approximately 50 ng NDMAFP (50 ng NDMAFP/mg polyDADMAC or 0.0085% molar yield) (10 polymer concentrations, linear fit, $R^2 = 0.98$). Although the polymer dose was high for many of the bench-scale samples, the "yield" of NDMA from polymer addition remained similar to that seen at the pilot plant (62 ng NDMAFP/mg polyDADMAC). No evidence indicated that an optimum polymer dose exists with regard to minimizing NDMAFP because NDMA formation always increased directly with increasing dose (i.e., higher polymer doses always increased NDMAFP).

In separate bench-scale experiments using CAP water, the polyDADMAC dose was held constant at 1.5 mg/L polyDADMAC (active polymer), and seven different brands/models of polymer were used in jar tests with alum (Figure 4). The NDMA yield of the settled water after polymer addition was 47 ± 3 ng NDMA/mg polyDADMAC (0.008% molar yield). DOC, UV_{254}, and NDMA yield were similar across all polymer sources.

When the polyDADMAC samples were diluted in ultrapure water and NH_2Cl was applied, the mean NDMAFP was 129 ng (standard deviation = 15 ng) NDMA/mg polyDADMAC (0.02% molar yield) and displayed greater variability in yield than the yield after coagulation with surface waters (Figure 4). This indicates that approximately one-third (average NDMA yield after settling/average polyDADMAC NDMA yield in ultrapure water) of the polyDADMAC NDMA precursors are not removed during the coagulation process in the presence of aluminum sulfate and natural water matrixes. Lee and Westerhoff (2006) previously showed that more dissolved organic nitrogen is removed during alum coagulation with polyDADMAC than is added (the polymer contains organic nitrogen) as long as a threshold (overdose) is not exceeded; about two thirds of the polyDADMAC-derived NDMA precursors were removed in this study. Overall, the pilot- and bench-scale coagulation experiments with multiple polymers and doses showed that use of polyDADMAC always increases NDMA formation.

FIGURE 4 NDMAFP yields of selected commercially available polyDADMAC polymers (one polyamine)



CAP—Central Arizona Project, DI—deionized, NDMAFP—*N*-nitrosodimethylamine formation potential, polyDADMAC—polydiallyldimethylammonium chloride

*Polydyne, Riceboro, Ga.
†Sterling Water Technologies, Columbia, Tenn.
‡CalChem Enterprises, Modesto, Calif.

Clarifloc® C-308P is shown twice because it was obtained from two separate treatment plants. The five error bars show one standard deviation of triplicate samples. Molar yield assumes the polymer as monomeric and does not apply to the polyamine, which has a molecular weight of 102 g/mol monomer (molar yield of 0.006 and 0.046% for jar-tested and diluted polyamine samples, respectively).

Removal of polymer-derived precursors by PAC. During an experiment at the pilot plant to determine whether PAC could remove polyDADMAC-derived precursors, one treatment train received PAC upstream of coagulation whereas the other received PAC and polyDADMAC simultaneously in the coagulation basin. The difference in NDMAFP across the entire treatment train between the train receiving PAC with coagulant and the train receiving PAC upstream was less than 4 ng/L, independent of PAC dose (ranging from 3 to 20 mg/L); this indicated that the point of PAC application does not strongly affect NDMA precursor removal and that PAC does not remove polyDADMAC-derived precursors when used during coagulation (Table 3).

Jar tests using Ohio or CAP water were performed using metal salts and polyDADMAC (10 doses from low to extremely high; 0.1 to 25 mg/L active ingredient). The settled supernatant was then removed and treated with PAC (3 to 20 mg/L). NDMAFP decreased after some PAC additions but increased after others. The increase or decrease in NDMAFP was independent of water source, PAC dose, and polyDADMAC dose but typically was less than the variability of the control samples. Although there were some small changes in NDMAFP after polymer and PAC treatment, it was difficult to delineate between removal of small amounts of polyDADMAC-derived precursors and watershed-derived precursors (i.e., Eq 1), whereas polymer-derived precursors dominated this water, based on NDMAFP after polymer addition (26 to 1,600 ng/L) compared with raw water NDMAFP (9 to 15 ng/L).

To further investigate removal of polyDADMAC-derived precursors at bench scale, experiments were conducted in which polyDADMAC was diluted with ultrapure water (0.1, 1.5, and 2.5 mg/L polyDADMAC [active polymer]) and mixed with PAC (3 and 20 mg/L) for 1 h. Figure 5 shows the NDMAFP of polymer-associated precursors after exposure to PAC at bench scale. For the triplicate samples conducted (0 and 20 mg/L PAC at 0.1 and 2.5 mg/L polyDADMAC), the NDMAFP of samples with PAC did not significantly differ from polymer-only samples at any polyDADMAC dose (Tukey's HSD, $p < 0.05$). This work showed that at bench and pilot scale PAC did not adsorb polyDADMAC-associated precursors well.

When polyamine (rather than polyDADMAC) was diluted in ultrapure water (polyamine was sampled from a treatment plant, premixed with coagulant) and contacted with PAC, the polymer-associated precursors sorbed well. Without PAC, the NDMAFP of 1 mg/L polyamine (4 mg/L coagulant) was 340 ng/L (yield = 340 ng NDMA/mg polymer) as shown in Figure 4; these results were higher than those for polyDADMAC and similar to the findings of Park and colleagues (2009). In jar tests with CAP water, polyamine yielded 43 ng NDMA/mg polymer and indicated that much of the precursor material was settleable, which was similar to polyDADMAC. However, adding PAC doses of 3 or 20 mg/L to ultrapure water containing 1 mg/L active polyamine achieved 76 or 96% removal, respectively, of NDMAFP (untreated NDMAFP = 340 ng/L); this was in stark contrast to polyDADMAC, which does not adsorb to PAC and is noteworthy because of the highly charged nature of both polymers. Compared with polyDADMAC-derived precursors, polyamine-derived precursors also settled better. In jar tests with CAP water, 87% of polyamine-derived precursors were removed during settling, compared with ~ 67% of polyDADMAC-derived precursors. To confirm these results, the sorption of polyamine should be further investigated with a polymer sample that is not premixed with coagulant.

TABLE 3 Difference between pilot-plant treatment trains with regard to point of PAC application

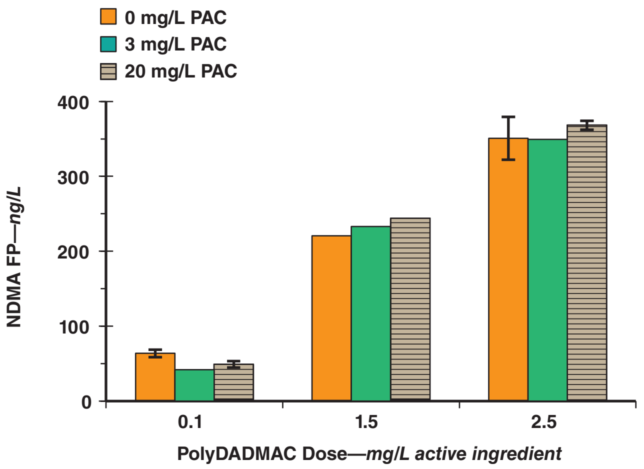
Polymer Dose *mg/L active polymer**	PAC Dose *mg/L*	Point of PAC Application Relative to Coagulation	Increase in NDMAFP Across Treatment Train *ng/L*
0.4	3	Upstream	29
0.4	3	Concurrent	25
0.4	20	Upstream	38
0.4	20	Concurrent	34

NDMAFP—*N*-nitrosodimethylamine formation potential, PAC—powdered activated carbon

*Based on bulk polymer containing 20% active polymer

PAC was added upstream of polymer addition or at the same time as polymer addition. Data are averages of duplicate samples. Influent NDMAFP ranged from 12 to 15 ng/L.

FIGURE 5 NDMAFP of polymer-associated precursors after exposure to PAC at bench scale



NDMAFP—*N*-nitrosodimethylamine formation potential, PAC—powdered activated carbon, polyDADMAC—polydiallyldimethylammonium chloride

PAC was contacted for 1 h in ultrapure water at 100 rpm using a gang stirrer. Error bars show one standard deviation of triplicate samples.

In one test to investigate oxidative removal of polymer-derived precursors, polyDADMAC (1.5 mg/L active polymer) was diluted in ultrapure water and contacted with free chlorine. After 24 h, residual free chlorine was measured (< 0.4 mg/L as Cl_2) before NDMAFP tests were conducted using preformed NH_2Cl. Applied free chlorine at 0.2, 0.5, and 1.0 mg/L as Cl_2 reduced NDMAFP from the polymer from 180 ng/L to 110, 100, and 60 ng/L, respectively. The lower chlorine doses likely dissipated in much less than the 24-h hold time. Recently published data offer further evidence of the possibility that polyDADMAC-derived precursors may be preoxidized by long contact times and high levels of exposure (Krasner et al, forthcoming; Shah et al, 2012).

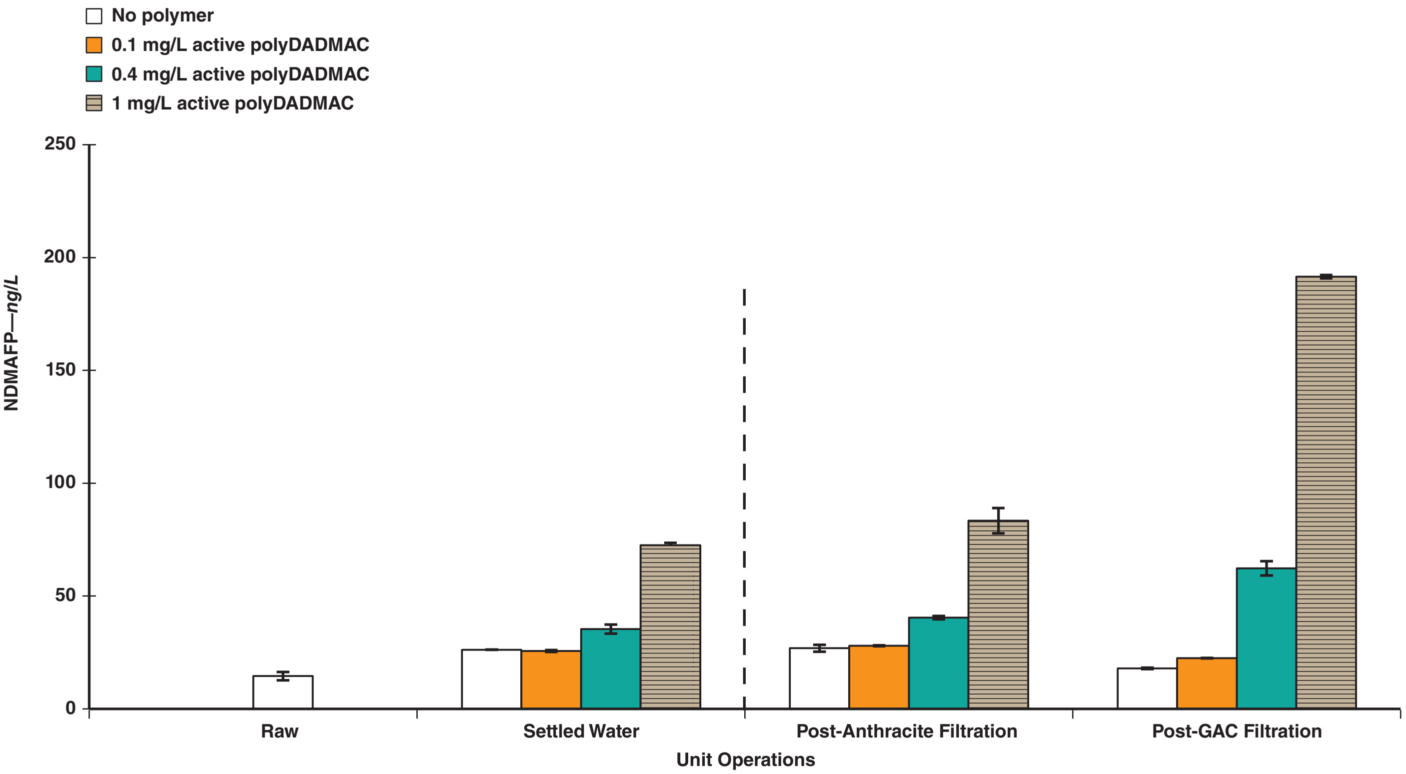
Moreover, as part of the pilot-plant testing, simulated distribution system (SDS) tests were conducted on the anthracite filter effluents, with a 20-min free chlorine contact time before ammonia addition (similar to that used at the full-scale plant). This resulted in NDMA formation of 3.6 ± 0.7, 6.0 ± 2.0, and

9.2 ± 0.8 ng/L for the 0.1-, 0.4-, and 1-mg/L polymer doses (active ingredient), respectively; the SDS NDMA formation with no polymer was 2.8 ± 0.5 ng/L. For the tests with 0.4 and 1.0 mg/L of polymer (active ingredient), the SDS NDMA yields (formation above that in the tests with no polymer) were 8.2 ± 4.7 and 6.4 ± 0.7 ng/L, respectively. These yields were likely lower than NDMAFP yields because of the destruction, transformation, or inactivation of precursors by preoxidation and lower NDMA formation under SDS conditions. Thus, free chlorine oxidation seems more effective at reducing NDMAFP from polyDADMAC than physical removal by AC. The combination of watershed-derived precursor removal from PAC and precursor loading from polyDADMAC use can be separated in the field if the addition of PAC and polymer occur in sequential unit processes, as was done at the pilot-scale plant.

Removal of polymer-derived precursors by GAC. Pilot tests without PAC but with polymer were conducted to assess removal of polymer-derived precursors by GAC. When the polyDADMAC dose was low (0.1-mg/L active polymer) or zero, the NDMAFP of the water increased from 16–19 ng/L in the raw water to 25–26 ng/L in the settled water (Figure 6); as shown in the figure, the NDMAFP of the polymer-affected sample was no different than that of the control sample. The NDMAFP of the GAC-filtered water with low polymer dose was 6 ng/L less than that of the anthracite-filtered water (22 versus 28 ng/L; all pilot plant samples taken in duplicate and averaged, replicates within ± 0.3 ng/L of the averages). Thus, when the polymer dose was low, GAC was able to remove some precursors, likely those of watershed origin. NDMAFP increased to 35 and 72 ng/L in the settled water for moderate and high polyDADMAC doses—i.e., 0.4 and 1 mg/L polyDADMAC (active polymer)—which corresponded to increases of 9 and 46 ng/L, respectively, compared with the settled water with no polymer, and increased further to 62 and 192 ng/L after GAC filtration. In contrast, for anthracite-filtered samples, the NDMAFP did not increase across the filter (Figure 6). Therefore, at the pilot plant only, when polyDADMAC-derived precursors were present, GAC exacerbated the potential for NDMA formation, particularly at elevated polyDADMAC doses. However, this could not be replicated at bench scale or at other full-scale plants (discussed subsequently).

Three other full-scale treatment plants using GAC and polyDADMAC as a coagulant aid were sampled twice to try to

FIGURE 6 NDMAFP across multiple unit operations at the pilot plant



GAC—granular activated carbon, NDMAFP—*N*-nitrosodimethylamine formation potential, PAC—powdered activated carbon, polyDADMAC—polydiallyldimethylammonium chloride

Raw water was coagulated with or without use of polyDADMAC and then settled and filtered with either anthracite or GAC. The bar labeled "Raw" is an average of raw water NDMAFP during the four conditions tested (error bar shows one standard deviation). Other data points are an average of duplicate samples with bars showing the individual samples. No PAC was used.

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observe this phenomenon. Two of the plants used F400[1] for TOC removal (EBCT = 20 and 21 min, respectively); at these plants, polyDADMAC doses of between 0.15 and 0.26 mg/L of polyDADMAC (active polymer) were used on the days of sampling. No increase was found in NDMAFP across GAC filters (300–19,000 bed volumes since replacement) at either treatment plant. In fact, NDMAFP decreased from 17 to 4 ng/L at one plant and from 14 to 5 ng/L at the other. The polyDADMAC doses were lower at these full-scale utilities than at the pilot plant and the conditions and use of the GAC were different.

At the third full-scale plant, which also used F400 (EBCT = 3.8 min), the doses were 5 and 6 mg/L polyDADMAC (active ingredient). During the first sampling, the polymer dose was 6 mg/L; at this dose, NDMAFP stayed the same or decreased across the GAC (from 152 ng/L in the settled water to 153 and 127 ng/L in the two absorber effluents, which had been in use for three years and one year, respectively). The NDMAFP of the raw water was 57 to 73 ng/L, so the GAC influent was a mixture of watershed- and polymer-derived precursors. In the second sampling, however, the polymer dose was 5 mg/L, and NDMAFP increased from 155 ng/L in the settled water to 253 and 311 ng/L, respectively, in the two absorber effluents. The absorbers had been in service for two and 15 months, respectively, and in this sampling, the NDMAFP of the raw water was 61 to 76 ng/L. As noted previously, both filters were spent in terms of TOC removal (15% removal).

To further investigate this potentially important phenomenon, a bench-scale GAC absorber was constructed using virgin GAC. Ultrapure water with 5 mg/L polyDADMAC (active polymer) was loaded for 11,000 bed volumes while the NDMA and NDMAFP of the effluent were measured. No NDMA was formed in the column (effluent NDMA); therefore, any NDMA formation at the pilot plant was unlikely to be through a "surface-catalyzed" reaction pathway as described by Padhye and colleagues (2011). With the exception of a single outlier sample that was not taken in replicate, NDMAFP in the effluent (effluent FP) also did not increase (number of samples = 12).

The situation in which NDMAFP increased across the GAC filters receiving polyDADMAC-treated water could not be replicated in the lab and remains a conundrum. However, the samples from the pilot plant and full-scale plant were in duplicate, and therefore the authors do not believe this to be erroneous data. It is possible that increasing NDMAFP across GAC contactors could be specific to the plants used in this study (river flow and turbidity nearly doubled from 21 to 42 ntu during the two days of the pilot-plant tests) or specific to GAC that has been in use for a long time, with intermittent polymer use at the pilot plant. Although turbidity was higher in the influent of the GAC column during the second day of polymer testing at the pilot plant (when high-polymer-dose, anomalous testing was completed), both the anthracite and GAC filter effluent turbidity decreased from 4 to 9 ntu (filter influent) to 0.04 ntu (anthracite or GAC filter effluent). Clarification of the mechanism of increasing NDMAFP across GAC filters at high polyDADMAC doses requires additional work (presuming that this phenomenon can be replicated).

DISCUSSION

Sorption of polymer-associated NDMA precursors. The dominant moiety in polyDADMAC is a positively charged amine group, which is responsible for bridging and settling negatively charged NOM during coagulation. The polymer is positively charged at typical water treatment (pH 8-adjusted log octanol–water partition coefficient, or K_{ow}, [log D] is much less than 0 and decreases with increasing polymerization); chemical drawing software (Chemicalize.org, 2013) was used for drawing, displaying, and predicting log D of the chemical structure. Given that the polymer itself is positively charged and that electrostatic interactions have greater energy than hydrophobic interactions (Crittenden et al, 2012), the authors did not expect physisorption to dominate.

Unlike polyDADMAC, however, polyamine does sorb to AC, and therefore, another mechanism must be at hand. The inclusion of hydroxyl (OH) groups in the polyamine repeating chain structure may explain the affinity for sorption given that polyDADMAC contains no oxygen. Hydrogen bond acceptors exist as oxygenated groups (e.g., phenolic, protonated carboxyl, carbonyl) along the planar sheet edges in AC, which exist in greater concentrations than simply negatively charged, deprotonated carboxyl groups required to attract the positively charged amine. However, inclusion of the OH group also increases the participation of hydrogen bonding with water. The N chain ends contained in polyamine but not in polyDADMAC have a lone electron pair that could be deprotonated at pH 8 (pK_a ~ 8), further contributing to the electrophilic nature of the molecule, and this also might explain the adsorption characteristics of polyamine (Chowdhury et al, 2012; Mattson et al, 1969).

Sorption of watershed-derived precursors. For bulk NOM, matrix effects (competition) may play a role in sorption affinity. Larger molecules at high concentrations (mg/L levels)—such as NOM—tend to block pores and thus make active sites within them unavailable for further sorption, whereas small molecules at trace concentrations—such as pharmaceuticals and anthropogenic chemicals—tend to be greatly outnumbered by active sites on the carbon surface. As shown in Figure 3, as the concentration of wastewater is increased, the NDMA precursor concentration increases as well. However, the percentage of precursors removed remains nearly the same. This is similar to previous research that found that percent removal of trace organic molecules is independent of initial concentration (Knappe et al, 1998) and to other work showing that as PAC dose increases, trace organic matter removal increases, independent of initial concentration of the trace organic matter (Li et al, 2005).

The same observation as with PAC was observed in the pilot-scale results in which the GAC columns were expended for DOC and UV_{254} removal but still removed NDMA precursors. DOC and UV_{254} removals less than that of NDMA precursors were also observed in previous research using rapid small-scale column tests (Hanigan et al, 2012). Previously, > 85% sorption of NDMA precursors was observed, whereas the pilot plant sorbed and/or biodegraded only ~ 30%. This was attributed to the exhaustion of the GAC, even for trace contaminants, as has been shown before on preloaded (exhausted) GAC (Knappe et al, 1999).

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Relative effects of AC and polymer use on NDMA formation. Eq 1 was developed to represent the conceptual differences in reactivity and treatability of watershed and polymer-derived NDMAFP. For example, influent NDMAFP at the pilot plant ranged from 9 to 19 ng/L, and PAC (3–25 mg/L) in the presedimentation basin reduced NDMAFP by 4 to 17 ng/L. Given that 0.4 mg/L polyDADMAC (active polymer) has the potential to increase NDMAFP ~ 9 ng/L relative to alum coagulation alone, removal of watershed-derived precursors by PAC may result in no net effect on the NDMAFP in this scenario. Any dose of polyDADMAC at a concentration greater than ~ 0.4 mg/L (active polymer) could cause a net increase in NDMAFP at the pilot plant. Many plants (including the full-scale plant associated with this pilot plant) use PAC seasonally for taste-and-odor issues when river flow and turbidity are low, and because of the low turbidity, many times no polyDADMAC is used concurrently. Assuming that PAC can remove polyamine- and watershed-derived precursors simultaneously and that PAC was fed into the coagulation basin, sorption of precursors by PAC could result in reduced settled water NDMAFP from both sources.

Table 4 gives the estimated Freundlich parameters and yield ranges for the remaining variables. Figure 7 shows the data from which Freundlich parameters were estimated. The Freundlich 1/n for watershed-derived precursors is greater than one, which is counterintuitive for strongly sorbed organic matter. The authors believe this is attributable to there being two groups of watershed-derived precursors represented by a single 1/n: one group is strongly sorbed at low PAC concentrations and the other is not sorbed well, independent of dose. This is similar to the authors' previous findings conducted with secondary wastewater effluent in which ~ 5% of NDMA precursors were not removed, even at PAC doses > 75 mg/L (Hanigan et al, 2012). However, these parameters are not broadly applicable to all treatment scenarios, and site-specific testing must be conducted.

The current study showed that polyDADMAC-derived precursors are not sorbable by AC, and therefore η_{pDMC} is set to zero. $NDMAFP_{WS}$ is dependent on source water precursor loading, whereas $NDMAFP_{pDMC}$ and $NDMAFP_{pAMN}$ are functions of dose and yield.

Figure 8 is a graphical representation of Eq 1 that is based on results from the current study. In Figure 8, the authors used influent and polyDADMAC-derived precursor loadings from the pilot plant, 15 ng/L NDMAFP, and 62 ng/mg active polymer (based on high polymer dose in which less polyDADMAC settled and likely a worst-case scenario). Polyamine contribution was 43 ng/mg active polymer. Removal of watershed- and polyamine-derived precursors follows the Freundlich functions in Table 4.

Overall, Figure 8 demonstrates the complexity of understanding how to control NDMA precursors. In this modeled example, achieving a final NDMAFP of 10 ng/L or less could be achieved by any of the following four approaches: not using polymer but using a low dose of PAC, using 0.1 mg/L active polyDADMAC and 13 mg/L PAC, using 0.1 mg/L active polyamine and 1 mg/L PAC, or using 0.25 mg/L active polyamine and 2 mg/L PAC. (These are theoretical data that have not been directly confirmed.) Alternatively, prechlorination could be explored.

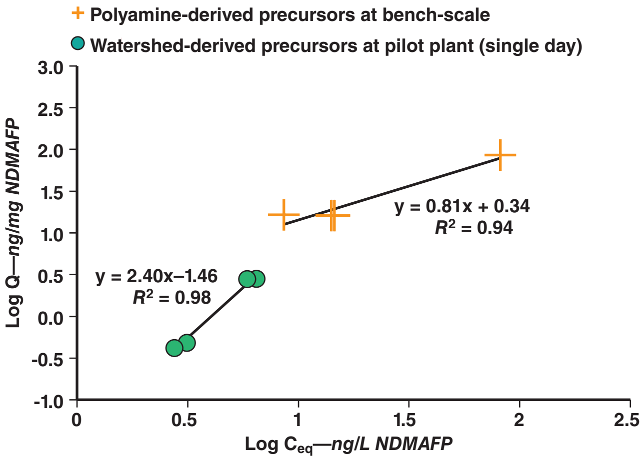
TABLE 4 Eq 1 estimated parameters

Sorption Variables	K (ng/mg)(L/ng)$^{1/n}$	1/*n*	R^2
η_{WS}	0.035	2.400	0.98
η_{pDMC}	Not sorbed	Not sorbed	Not sorbed
η_{pAMN}	2.197	0.8129	0.94
Yield Variables	**Postsedimentation Yield**		R^2
$NDMAFP_{WS}$	0–100 ng/L		NA
$NDMAFP_{pDMC}$	47–62 ng NDMAFP/mg active polyDADMAC		0.98–0.99
$NDMAFP_{pAMN}$	43 ng NDMAFP/mg active polyamine		1*

η—dose-dependent percent removal of precursors by activated carbon, NA—not applicable, NDMAFP—*N*-nitrosodimethylamine formation potential, p_{AMN}—polyamine-derived precursors, p_{DMC}—polyDADMAC-derived precursors, polyDADMAC—polydiallyldimethylammonium chloride, WS—watershed-derived precursors

*Only two doses tested

FIGURE 7 Freundlich isotherms for watershed- and polyamine-derived NDMA precursors



NDMA—*N*-nitrosodimethylamine, NDMAFP—NDMA formation potential

Watershed data shown are from a single day because of temporal variability in precursor adsorption.

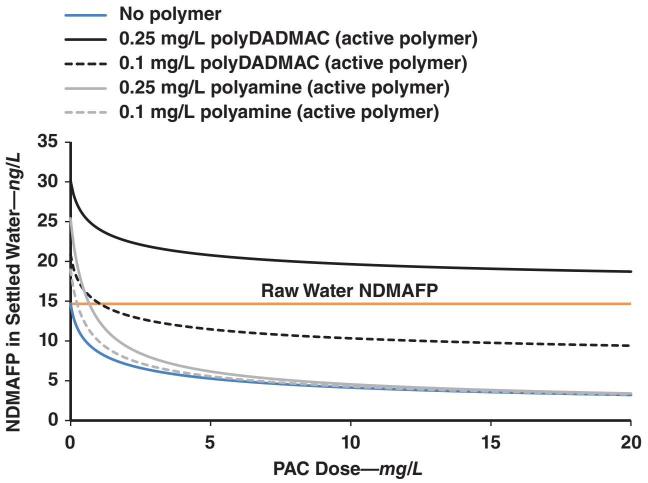
Both polyamine and watershed datasets contain four data points (two polyamine data points overlapping).

CONCLUSION

This study investigated the removal of polyDADMAC- and watershed-associated NDMA precursors by both PAC and GAC.

- Precursors were removed well by both PAC (up to 82% removal at a dose of 20 mg/L PAC) and GAC, even on GAC columns that were expended for DOC removal (31% precursor removal), although it is possible that some precursors removed by GAC were derived in the pilot plant itself (7 ng/L NDMAFP increase across sedimentation when no polymer was used).

FIGURE 8 Conceptualization of NDMA precursor contribution and removal in the pilot plant



NDMA—*N*-nitrosodimethylamine, NDMAFP—NDMA formation potential, PAC—powdered activated carbon, polyDADMAC—polydiallyldimethylammonium chloride

- Contact times longer than 15 min with PAC relevant within drinking water treatment did not significantly affect removal of watershed-derived precursors.
- Percentage removal of watershed-derived precursors remained constant, independent of changes in influent precursor loadings.
- PolyDADMAC reactivity in forming NDMAFP after simulated alum and polymer coagulation was 47 ng NDMAFP/mg active polyDADMAC, which was about one-third the NDMAFP of the polymer diluted in ultrapure water, indicating that much of the polymer-derived precursors were removed during settling.
- Polyamine reactivity after jar tests was 43 ng NDMAFP/mg active polyamine (13% of yield when diluted in ultrapure water), indicating the potential for better removal during coagulation than polyDADMAC-derived precursors.
- PolyDADMAC-derived precursors were not removed to an appreciable extent by either PAC or GAC, but polyamine-derived precursors were removed well (up to 75% when mixed with PAC in ultrapure water).
- Oxidation with free chlorine was effective at reducing NDMAFP from polyDADMAC-derived precursors.
- At a pilot plant in this study, it was found that use of greater than 0.4 mg/L of active polyDADMAC would cause a net increase in NDMAFP leaving the treatment plant, despite the use of PAC in a presedimentation basin to remove watershed-derived precursors.
- Strategies other than sorption to AC are required to mitigate NDMA formation in treatment plants using polyDADMAC (e.g., preoxidation).

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PEER REVIEW

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FOOTNOTES

[1] Calgon Carbon, Pittsburgh, Pa.
[2] Polydyne, Riceboro, Ga.
[3] Sterling Water Technologies, Columbia, Tenn.
[4] CalChem Enterprises, Modesto, Calif.
[5] Whatman, Maidstone, United Kingdom
[6] PB-900, Phipps & Bird, Richmond, Va.
[7] Cabot Norit Americas, Marshall, Texas
[8] General Chemical, Parsippany, N.J.
[9] Barnstead™ Nanopure™, Thermo Scientific, Waltham, Mass.
[10] Fisher Chemical, Fair Lawn, N.J.
[11] Sigma Aldrich, St. Louis, Mo.
[12] Monochlor F, Hach, Loveland, Colo.
[13] DR 5000, Hach, Loveland, Colo.
[14] TOC-V$_{CSH}$ with attached TNM, Shimadzu, Kyoto, Japan
[15] Multispec-1501, Shimadzu, Kyoto, Japan

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