Purification and removal of the low molecular weight fraction of PolyDADMAC reduces N-nitrosodimethylamine formation during water treatment

Journal:	*Environmental Science: Water Research & Technology*
Manuscript ID	EW-ART-04-2020-000392.R1
Article Type:	Paper

Nitrosamines form in the presence of chloramine disinfectants during drinking water treatment. Drinking water treatment relies upon chemical addition, including cationic polymers (e.g., polyDADMAC), to achieve turbidity and pathogen removal. The present study shows the contributions of cationic polymer to nitrosodimethylamine (NDMA) formation, and how polyDADMAC purification can dramatically reduce NDMA formation. Diaultrafiltration of polyDADMAC to remove low molecular polymer residuals reduced NDMA formation by over greater than 50% without impacting other water treatment goals.

Purification and removal of the low molecular weight fraction of PolyDADMAC reduces N-nitrosodimethylamine formation during water treatment

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Abstract

Cationic polymers are critical coagulant aids at drinking water plants, but the same polymers are simultaneously N-nitrosodimethylamine (NDMA) precursors upon chloramine exposure. We hypothesized the low-molecular fraction, which represents a small mass residual in polyDADMAC cationic polymer, reacts with chloramines, may not be well removed during coagulation, and is thus responsible for forming parts-per-trillion (ppt) concentrations of NDMA in finished water. To identify strategies capable of reducing post-coagulation residual polymer associated with NDMA formation, this study fractionated polyDADMAC by molecular weight, characterized reactivity of each fraction, and quantified precursor contributions to NDMA formation potential during bench-scale test and NDMA concentration due to formation during treatment during pilot tests. Diaultrafiltration of the cationic polymer produced a low molecular weight fraction (<10 kDa) and a purified polyDADMAC (>10 kDa). Native organic matter in bench- and pilot- tests contributed 19–38% of NDMA formed throughout treatment, while polymers were responsible for 62–81% of NDMA formed. The <10 kDa fraction of polyDADMAC was more reactive (450–540ngNDMA/mgDOC) and formed >10x NDMA than non-purified polyDADMAC in jar tests. Purified polyDADMAC, with <10 kDa fraction removed, formed 54% less NDMA during pilot tests (and 63% less during jar tests) than non-purified polyDADMAC. There was no adverse effect on coagulation or subsequent filter performance by using purified polyDADMAC, but significantly ($p<0.05$) less NDMA formed in filtered water when using diaultrafiltered cationic polymer. Thus, removing the low molecular weight impurities (<10 kDa) by polymer suppliers would lead to an equally-effective coagulant-aid that substantially lowers NDMA formation during drinking water treatment.

Keywords: N-nitrosodimethylamine, disinfection by-products, coagulation, precursors

Introduction

Nitrosamines are potential carcinogens and disinfection by-products in drinking water.[1] N-nitrosodimethylamine (NDMA) is the most frequently detected and highest concentration nitrosamine produced during chloramination of drinking waters.[2,3] NDMA is part of the United States Environmental Protection Agency (USEPA) contaminant candidate list 4 (CCL4), and regulatory limits exist for drinking water at concentrations of 10 to 40 ng/L in several states and countries (e.g., Canada, Australia, Massachusetts, California). Organic NDMA precursors include natural organic matter, trace organics in wastewater, and cationic polymers used as coagulant aids in water treatment plants.[2,4] Polydiallyldimethylammonium chloride (polyDADMAC) is the most commonly used cationic polymer, used in approximately 60% of water treatment plants in the US, and has been linked to significant NDMA formation.[5–7] Polyamines are the second most commonly used cationic polymer class. Polymeric coagulant aids contain long chain polymers, oligomers (i.e., short-chain polymers), polymer precursors (e.g., monomer), and impurities.[8–10] Low molecular weight organics, including dimethylamine (DMA) and diallyldimethyl ammonium chloride (DADMAC), present in polyDADMAC, have been identified as NDMA precursors but have yields of <1%.[5,10–13] We hypothesized that commercial polyDADMAC contains residual low molecular weight polymers from the manufacturing process and that these residuals or impurities (1) are irrelevant as coagulant aids (i.e., do not influence coagulation, sedimentation, or filtration of particulates), (2) are poorly removed during water treatment, (3) have higher NDMA reactivity (ngNDMA/mg polymer) than bulk polyDADMAC, and (4) are significant sources of NDMA in chloraminated drinking water.

To quantify the contribution of the different constituents, commercial polyDADMAC solutions were separated into a "purified" higher molecular weight fraction (>10 kDa) and a lower molecular weight fraction (<10 kDa) using dead-end and recirculation diaultrafiltration and then used in bench- and pilot-scale experiments simulating full-scale water treatment conditions. Bench-scale tests, measured NDMA formation potential (NDMAFP) and were used as proof-of-concept, that the removal of the <10 kDa fraction reduced NDMAFP. Pilot tests, were used to demonstrate at full-scale the reduction of NDMA formed during treatment when a purified (>10 kDa) polymer was used. The objectives of this study were to: (1) compare the NDMA formation potential (NDMAFP) reactivity of the polyDADMAC molecular weight fractions and combined fractions with reactivity and jar tests, (2) quantify the contribution of different molecular weight fractions to NDMA formed during treatment under realistic drinking water conditions with pilot tests, and (3) identify strategies that the polymer manufacturers and/or water treatment plants can use to minimize NDMA formation.

Experimental Methods

Polymer Sources, Fractionation, and Purification

Commercial cationic polymers were provided by a major chemical vendor (SNF Polychemie). During screening experiments comparing NDMA formation potential (NDMAFP) for Clarifloc C308 and C318, C308 produced roughly 70% less NDMA (Figure S1). Polyamines are the second most common polymeric coagulant aid used in water treatment facilities and are known sources of NDMA precursors. Two sources of polyamine polymers had higher NDMAFP than C308 (Figure S2). Therefore, because of the common use of C308 and the lower NDMAFP from the polymer upon chloramination, most experiments used C308 (20% active polymer).[6,11]

A 10kDa membrane was selected to fractionate the polymer based upon prior research,[5] and it was utilized in a either a dead-end cell (Amicon) or larger-scale recirculating diaultrafiltration system (Millipore Ultracel and Pellicon 10 kDa membranes). Each polymer fraction was analyzed for total organic carbon (TOC) and total dissolved nitrogen (TN) to ensure mass balance (TOC whole polyDADMAC= TOC >10 kDa + TOC <10 kDa) was within 10% and to inform dosing in subsequent reactivity, jar, and pilot tests. TOC is used to normalize results in reactivity and NDMAFP tests, as a surrogate for the active polymer mass.

The dead-end stirred cell operated at 50 psi was used to filter 400 mL of feed until 150 mL remained. The feed was rediluted to 400 mL with ultrapure water and filtered again. The concentrated feed was rediluted to 400 mL, and this solution was considered the bench-scale purified polyDADMAC (>10 kDa). The 500 mL of permeate collected throughout filtration was combined, constituting the bench-scale lower molecular weight fraction (<10 kDa). Separate experiments collected permeate from a 1 kDa ultrafilter membrane (termed <1 kDa fraction), and used in a limited number of experiments. The bench-scale fractions were used in reactivity and jar tests.

Prior to diaultrafiltration, Millipore Ultracel and Pellicon 10 kDa membranes (for bench- and pilot- scale, respectively) were cleaned by soaking in ultrapure water for 24 hours (with three water changes) and used to filter ultrapure water (200 mL and 10 L, respectively) that was discarded. C308 was diluted with ultrapure water (>18 $M\Omega.cm^{-1}$) to 10% active polymer concentration and used as the feed. A cross-flow filtration apparatus was used, with pressure being regulated by a valve on the concentrate stream. The concentrate was recirculated to the feed and continuously diluted with ultrapure water to maintain a constant feed volume of 45 liters. Filtration continued until 45 liters of permeate was collected (appx. 30 hours of continuous operation). The recirculated concentrate was termed “pilot-purified polyDADMAC (>10 kDa),” and the permeate was considered the “pilot low molecular weight fraction (<10 kDa)”.

Bench-Scale Jar Tests

Bench-scale experiments were conducted in a standard jar test apparatus (PB900, Phipps and Bird, Virginia, USA) with 5 and 30 minutes of rapid mixing and flocculation, respectively, followed by 60 minutes settling time.[14] Jar tests were performed with Colorado River Water (CRW) collected from the Central Arizona Project in Scottsdale (Arizona, USA). CRW has a low watershed NDMA formation potential and is useful to differentiate NDMA associated with polymer addition. Coagulation conditions—20 mg/L alum dosages and 2 mg/L polyDADMAC as active polymer—were selected to optimize particle and dissolved organic carbon removal and closely mimic full-scale water treatment conditions at the point of CRW collection. Three fractions of Clarifloc C308 polyDADMAC were utilized in the testing: (1) as-received, non-fractioned polymer, (2) low molecular weight fraction (<10 kDa), and(3) purified polyDADMAC (>10 kDa fraction). Turbidity in each jar was measured in triplicate. Supernatant samples were filtered (Millipore GF/F filters) prior to water quality analysis and NDMAFP tests.

Pilot-Scale Tests with Purified Cationic Polymers

Briefly, a two-train pilot-scale facility (Houston, TX) that replicates key full-scale facility operations (Figure S3) was operated using either the as-received C308 polyDADMAC or the purified higher molecular weight fraction (>10 kDa) polyDADMAC as the coagulant aid. Mimicking full-scale operations, the raw water consisted of 100% Trinity River water that was chloraminated at the plant intake through addition of sodium hypochlorite at 2.5 to 3 mg/L and liquid ammonium sulfate at 0.5 mg/L. Due to chloramination at the intake, NDMA could form across the treatment train through reaction between chloramines and the native water matrix, polymer added, or residual polymer (after sedimentation). The raw water was pumped into two parallel treatment trains where each treatment train included mixing and flocculation tanks where 35 mg/L ferric sulfate was added with either an optimized polymer dose condition (2.6 mg/L active polymer) or an overdosed polymer condition (5.2 mg/L active polymer). Following flocculation, process waters in each train flowed over a weir and into an upflow sedimentation tank. The settled water was lifted via pumping to two sand/anthracite filter columns per train. Raw, settled, and filtered water samples were collected from each train. Samples were analyzed for pH, temperature, turbidity, total chlorine, total ammonia, monochloramine residual, UV absorbance at 254 nm, TOC, and NDMA. Note, NDMA was directly measured, NDMAFP was not performed in pilot tests. With the exception of NDMA, there were no significant differences ($p>0.05$) in the water quality measurements between the two trains.

NDMA Reactivity and Formation Potential Test Conditions

To measure NDMAFP reactivity of polymer solutions were conducted using 10 mg/L active polymer with ultrapure water, and TOC was measured. NDMAFP of dilute polymer solutions and jar test effluent was measured in duplicate with 500 mL samples. These solutions were buffered to pH 8 with 10 mM borate buffer before dosing to 18 mg/L as Cl_2 with pre-formed monochloramine. Samples were sealed and left in the dark at room temperature for 72 hours, after which the residual monochloramine was measured (Monochlor-F reagent Hach kit) and was >3.5 mg/L for all samples. Samples were immediately quenched with ascorbic acid and spiked with 100 ng/L NDMA-d_6 internal standard. Samples were kept in the dark at 4° C until NDMA extraction and analysis could be performed.

Analytical Methods

NDMA extraction and analysis. EPA method 521was used for NDMA extraction and analysis. [15] Briefly, 500 mL sample was passed through a Restek EPA 521 charcoal solid phase extraction (SPE) cartridge after it was conditioned with dichloromethane (DCM), methanol, and high performance liquid chromatography (HPLC) grade water. After the sample was loaded, it was dried with nitrogen gas, and the organic compounds were eluted from the cartridge with DCM. The DCM extracts were blown down with nitrogen gas to 1 mL, dried using anhydrous sodium sulfate cartridges, and stored at -4° C. Extracts were analyzed with Agilent 6890N/5973 inert gas chromatography–mass spectrometry (GC/MS) in positive chemical ionization mode with Agilent DB-1701P (Santa Clara, CA) column, ammonia reagent gas, and He carrier gas. The column oven temperature was 40 °C for 3 minutes, increased by 4 °C per minute to 80 °C, and increased to 120 °C at 20 °C per minute. The column interface temperature was 200 °C. The mass selective detector analyzed mass-to-charge 92 (NDMA + NH_4^+) and 98 (NDMA-d_6 + NH_4^+). Calibrations were performed using a series of NDMA standards from 1 to 1000 µg/L, each with a 100 µg/L NDMA-d_6 internal standard.

^{1}H-NMR spectroscopy. To prepare samples for nuclear magnetic resonance (NMR), polymer solutions were freeze dried to remove all water. Samples were rapidly frozen in a -80 °C freezer then dried using a LABCONO Free Zone freeze dryer, which kept samples at -57 °C and 0.47 mbar for 24-48 hours until all water was removed from the sample. All samples were prepared in D_2O with 0.05 wt.% 3-(trimethylsilyl)propionic-2,2,3,3-d_4 acid and sodium salt (TSP) as an internal reference. Proton NMR was performed on a Bruker 400 MHz spectrometer; a single pulse experiment was conducted on all samples.

Basic water quality analysis. Standard methods (USEPA, APHA) were used for pH, TOC, UV-254, bromide, turbidity, and other water quality parameters. Non-purgeable organic carbon (NPOC) and total nitrogen (TN) were measured using a Shimadzu TOC-L analyser with TN unit, after the pH of all samples, blanks, quality control samples, and calibration standards was adjusted to below pH 4.5 with hydrochloric acid. NPOC calibration standards were made with potassium hydrogen phthalate in ultrapure water in the range of 0.5 mg/L to 10 mg/L. TN standards were made with potassium nitrate in ultrapure water in the range of 0.1 mg/L to 5.0 mg/L. Blanks and quality control standards were run every 15 samples. NPOC of blanks were always measured as <0.5 mg/L, and quality control standards were within ±15% of expected concentration. Turbidity was measured using a Hach nephelometer, and pH was measured using an Omega bench-top probe and meter.

Statistical Analysis

Statistical significance tests were performed to compare NDMA concentrations formed and water quality under different test conditions. In general, a two-tail unpaired t-test assuming unequal variances was used ($\mu_1 \neq \mu_2$). Differences were considered to be significant for $p < 0.05$.

Results and Discussion

Fractionation, Characterization, and NDMAFP Reactivity of polyDADMAC Fractions

Figure 1 shows DOC and TDN of the polyDADMAC after separation into three molecular weight fractions. PolyDADMAC consists mostly of high molecular weight (>10 kDa) organics, with only 5–10% of the constituents in the <10 kDa fraction. In separate ultrafiltration tests, polymer material in the lowest molecular weight size fraction (< 1 kDa) was the most enriched in nitrogen (higher TDN/DOC ratios) compared against the higher MW fractions; material in the <1kDa fraction represents a subset of material in the separately performed <10kDa fraction. Therefore, because there were only minor mass differences for the <10 kDa and <1 kDa fractions and because the 10kDa ultrafilter had a much higher water permeate flux than the tighter membrane (1 kDa), all further experiments used only the 10 kDa ultrafilter, thus limiting the volume of purified polymer needed to meet the pilot-scale treatment polymer feed requirements.

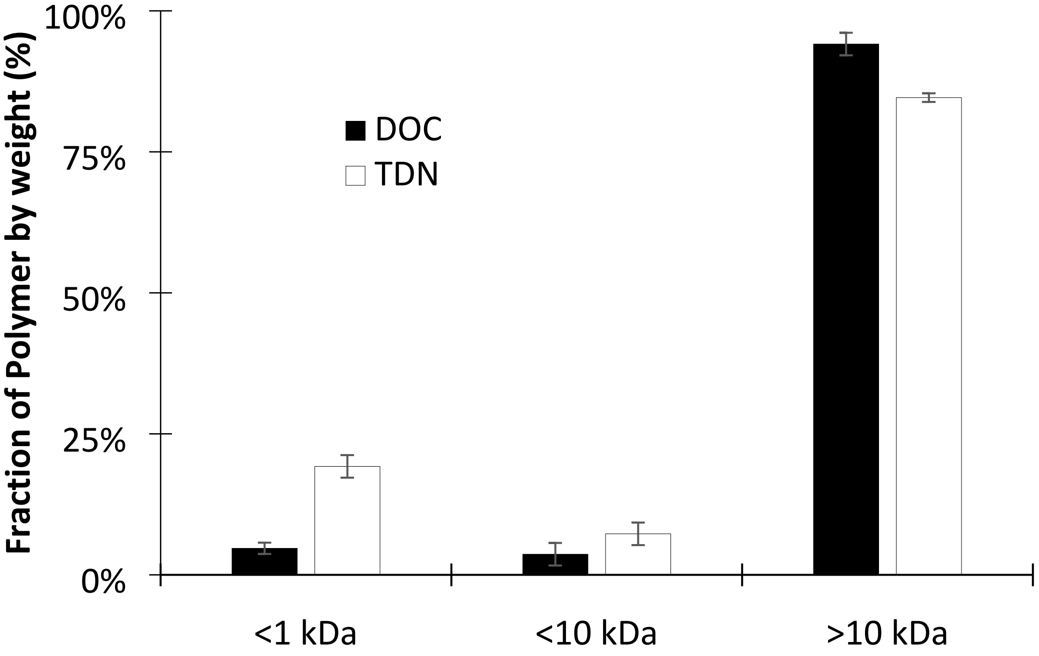

Figure 1 The organic (DOC) and nitrogenous (TDN) mass proportions of polyDADMAC by molecular size, with <1 kDa and <10 kDa fractions representing lower molecular weight constituents and >10 kDa representing higher molecular weight constituents.

Figure 2 shows the NDMAFP reactivity of the different polyDADMAC fractions. Non-purified polyDADMAC exhibited only slightly higher ($p>0.05$) reactivity (130 ngNDMAFP/mgDOC) than the >10 kDa fraction (115 to 120 ngNDMAFP/mgDOC) obtained from the dead-end and the recirculating diaultrafiltration processes. Note that the dead-end and recirculating diaultrafiltration processes had comparable reactivity, which is important because the recirculating system was needed to produce a large enough volume of purified polymer for the pilot tests. However, the low molecular weight (<10 kDa) fraction is four to five times more reactive (450 to 540 ngNDMAFP/mgDOC) than the non-purified polyDADMAC. In separate experiments with a polyamine cationic polymer, similar reductions in NDMA were observed comparing non-purified polymer solutions (720 ngNDMAFP/mg polymer) against 10 kDa purified polyamine solutions (380 ngNDMAFP/mg polymer) (Figure S2). This demonstrates the NDMA precursors are present in the <10 kDa fractions of different cationic polymers. While the <10 kDa fraction accounts for <10% of the DOC in the non-purified polyDADMAC (Figure 1), mass balance calculations suggest that the <10kDa fraction accounts for roughly 20 to 40 ngNDMA/mgDOC or 30-40% of NDMAFP in the non-purified polyDADMAC solution.

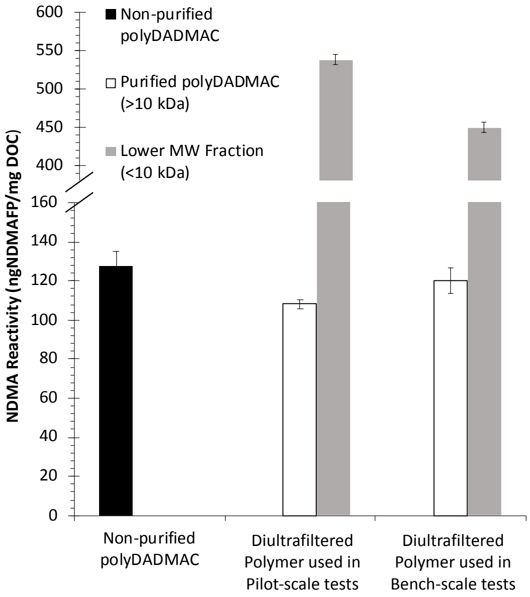

Figure 2 NDMAFP reactivity of the non-purified C308 polyDADMAC compared to the lower molecular weight fraction (<10 kDa) and purified (>10 kDa) polyDADMAC.

To identify why the NMDA FP varies in the different polyDADMAC fractions, ^{1}H-NMR was performed. Figure 3 shows the ^{1}H-NMR spectra for purified and non-purified polyDADMAC. A dimethylamine (DMA) peak at 2.73 ppm exists in the non-purified polyDADMAC, but not in the purified >10 kDa polyDADMAC. The DMA peak and peaks at 1 and 3 ppm are higher in the < 10kDa than non-purified polymer. The peaks at 1 and 3 ppm are of unknown identity, but they likely include more homogenous compounds than represented by broad NMR peaks and/or represent molecules with higher density of functionalized end-groups. DMA is important because it is thought to be a NDMA precursor.[9,12,13] Manufacturers report DMA ranging from 0.005 to 0.025 wt% (50–250 mg/L) in commercial polyDADMAC. ^{1}H-NMR spectra indicated that DMA was more prevalent (0.03–0.17%, 300–1700 mg/L) in the <10kDa fraction than the non-purified polymer. Reported NDMA yields from DMA range between 0.2% and 1.5%;[10,16] which translates to a NDMA reactivity of 0.2– 6.2 ng NDMA per mg-C for the non-purified polymer and 0.9–42 ng NDMA per mg-C for the <10 kDa fraction. Roughly 4% of the NDMA could originate from DMA in the non-purified polymer, and 8% in the < 10 kDa fraction. As supported by other studies,[10] DMA does not *fully* explain the significantly higher reactivity of the <10 kDa fraction of polyDADMAC. Furthermore, there are fewer peaks in the >10kDa fraction. The monomer DADMAC has also been reported by the manufacturer at concentrations up to 0.12% or 1200 mg/L in the polyDADMAC solutions, and peaks labeled with arrows in the <10 kDa fraction are indicative of the carbon double bonds in DADMAC. DADMAC is reported to have a much lower formation potential than DMA[10] and thus does not contribute substantially to NDMA formation. Finally, in the <10 kDa fraction there appear to be more polymer endgroups detected in the 1.0 to 1.2 ppm range. This makes sense as a greater number of end-groups, relative to the total number of molecules in solution, are expected for shorter-chain length organic molecules present in the <10 kDa fraction. Compared with data shown in Figure 2, while DMA could account for a portion of the NDMA reactivity, the results suggest that other un-identified polymer residuals also contribute to NDMA formation.

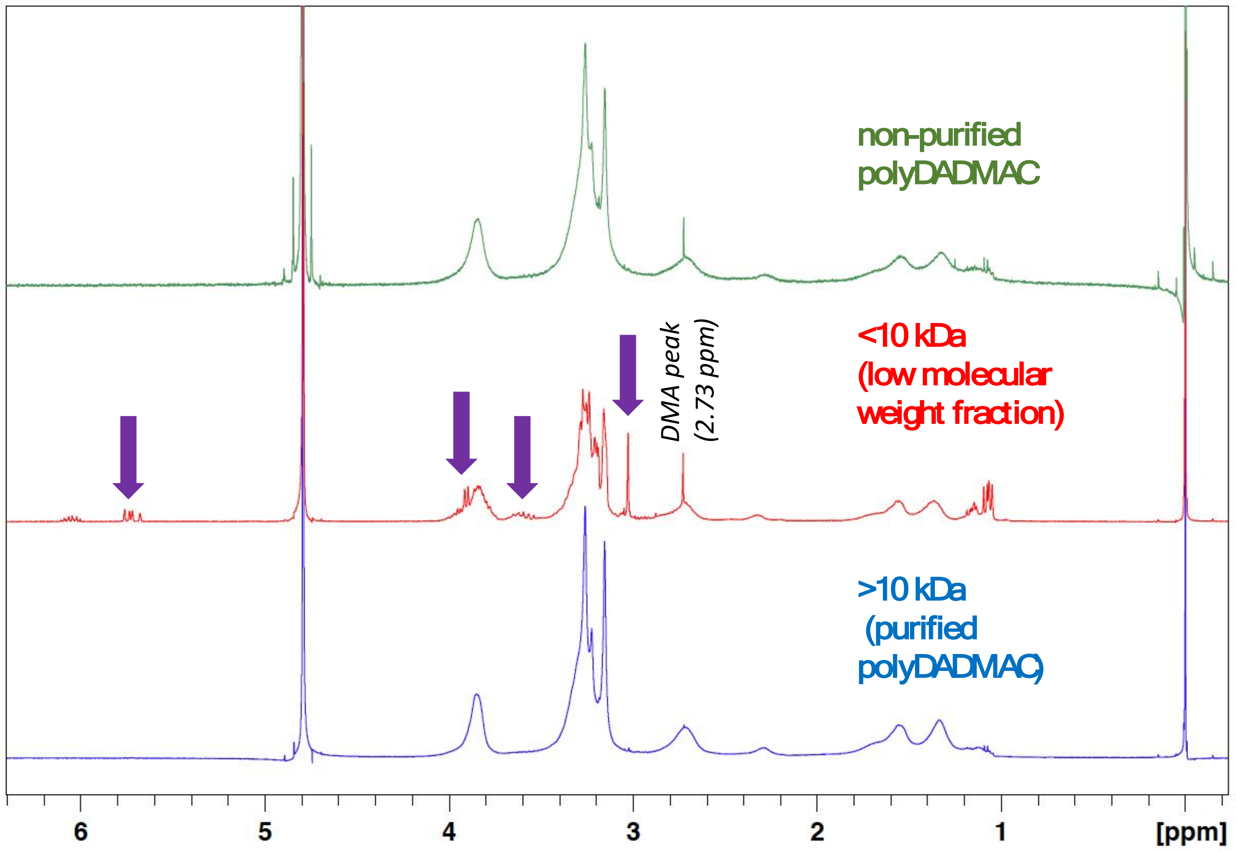

Figure 3 ^{1}H NMR spectra of non-purified C308 polyDADMAC (top in green), the low molecular weight <10 kDa fraction (middle in red), and the purified polyDADMAC >10 kDa fraction (bottom in blue). The location of the DMA peak at 2.73 ppm is shaded in each spectrum. Purple arrows in the low molecular weight <10 kDa fraction indicate peaks attributed to DADMAC. Peaks between 1.0 and 1.2 ppm are assocaited with polymer endgroups.

Contribution of PolyDADMAC Fractions to NDMA Formation During Jar tests

Jar tests without polymer and with the different polyDADMAC fractions were performed to evaluate their contribution to NDMA formation in natural waters. Residual turbidity in treated supernatant (i.e., after coagulation, flocculation, and sedimentation) was statistically (p>0.05) the same for treatments using non-purified, purified (>10kDa) solution, and <10 kDa fraction polyDADMAC (Figure S4) and was statistically better (>30% lower turbidity, $p<0.05$) compared against alum coagulation alone. These results demonstrate that all the polymer fractions enhanced particle removal.

Figure 4 shows NDMAFP in settled supernatant after jar testing. For alum coagulation alone, the native water matrix precursors produced 29 ngNDMAFP/L. Coagulation using alum plus non-purified polyDADMAC approximately doubled (1.6x) the NDMA formation, demonstrating that polyDADMAC significantly ($p<0.05$) contributes to NDMA formation. Coagulation using alum plus <10 kDa fraction of polyDADMAC formed 823 ngNDMAFP/L. This demonstrated the potential for the lower molecular weight fraction of polyDADMAC to contribute NDMA precursors during water treatment. Finally, coagulation was performed using alum coagulation plus a purified polyDADMAC, where the low MW fraction (<10 kDa) was removed via diaultrafiltration. The NDMA formation was 30 ng/L (62%) lower ($p<0.05$) than the non-purified polyDADMAC (Figure 4). This work demonstrated the feasibility for purified polyDADMAC (i.e., to remove <10 kDa fraction of polymer residuals) to achieve turbidity removal goals, and significantly reduce polymer-derived NDMA precursors present after coagulation.

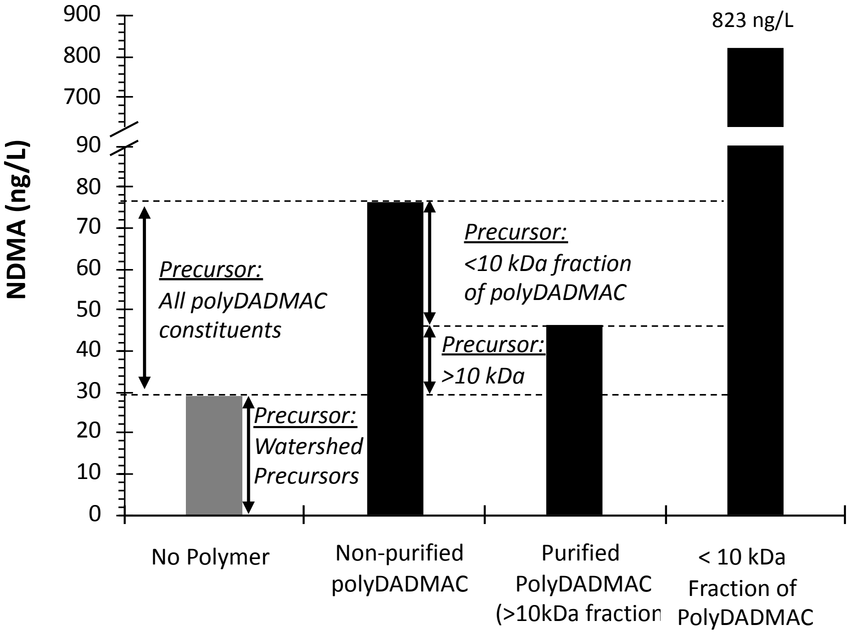

Figure 4 NDMA formed due to background watershed organics plus polymer precursors in Central Arizona Project water after coagulation (ferric chloride alone (No polymer) or with different polyDADMAC fractions), flocculation, sedimentation, filtration, and chloramination (18 $mgCl_2/L$).

Pilot Tests Confirmed Lower NDMA Formation using Diaultrafiltered PolyDADMAC

To evaluate purified polyDADMAC (>10 kDa) to reduce NDMA formation under realistic continuous-flow drinking water treatment plant conditions, pilot tests that mimicked the full-scale treatment processes were performed. Figure S5 shows the DOC (5 mg/L) is lower in the settled waters than the raw water (6.2 mg/L) and that DOC was the same whether purified or non-purified polyDADMAC was added. This result demonstrates purified polyDADMAC was as effective as the non-purified polyDADMAC as a coagulant aid. Furthermore, DOC after filtration was lower when using the purified polymer compared against non-purified polyDADMAC.

Figure 5 shows NDMA concentrations directly measured across the pilot treatment trains (not NDMAFP). Because there was a chloramine residual in raw water (see methods), NDMA formed during coagulation and other processes. NDMA in the raw water was 4.5 ng/L. In the presence of non-purified polyDADMAC, NDMA in settled and filtered waters was 15 and 24 ng/L, respectively. This illustrates a high contribution of NDMA from polyDADMAC. However, using the diaultrafiltered polyDADMAC (i.e., <10 kDa fraction removed) the NDMA in settled and filtered waters was 9 and 13 ng/L, respectively. Overall, the diaultrafiltered polyDADMAC reduced NDMA contributed by the polymer by 53%.

To further explore the relationship between NDMA formation and cationic polymer coagulant aids, pilot tests were run to compare optimal versus over-doses (*2x* optimal dose) of polyDADMAC. Cationic polymer overdosing can occur at a treatment facility if dose is not properly optimized or when the water flowrate varies but polymer feed pumps are not flow-adjusted. All conditions achieved comparable turbidity and DOC removals (not shown). Raw water NDMA averaged 4.5 ng/L throughout the tests. In agreement with trends for optimal polymer dosing, Figure 5 also indicates that polymer overdosing always led to higher NDMA across the pilot plant. Using purified (>10 kDa diaultrafiltered) polyDADMAC significantly ($p<0.05$) lowered NDMA compared against non-purified polymer. Polymer overdosing using the purified polyDADMAC only increased NDMA by 40% compared against a 61% increase in NDMA when non-purified polyDADMAC was overdosed. Optimal polymer dosing reduced NDMA concentrations in filtered water by 10 ng/L, and 19 ng/L during the polymer overdosing scenario. These are dramatic reductions in NDMA levels relative to existing standards. Clearly, utilities should avoid cationic polymer overdosing as a strategy to reduce NDMA in finished water. Additionally, polymer purification has substantial opportunities to limit NDMA formation in finished water. Further optimization of the purification process can likely achieve even greater reductions in low molecular weight NDMA precursors. While these results confirm the dependence of NDMA on polymer addition, they also demonstrate the efficacy of using diaultrafilter-purified polyDADMAC to reduce NDMA formation under actual operation conditions.

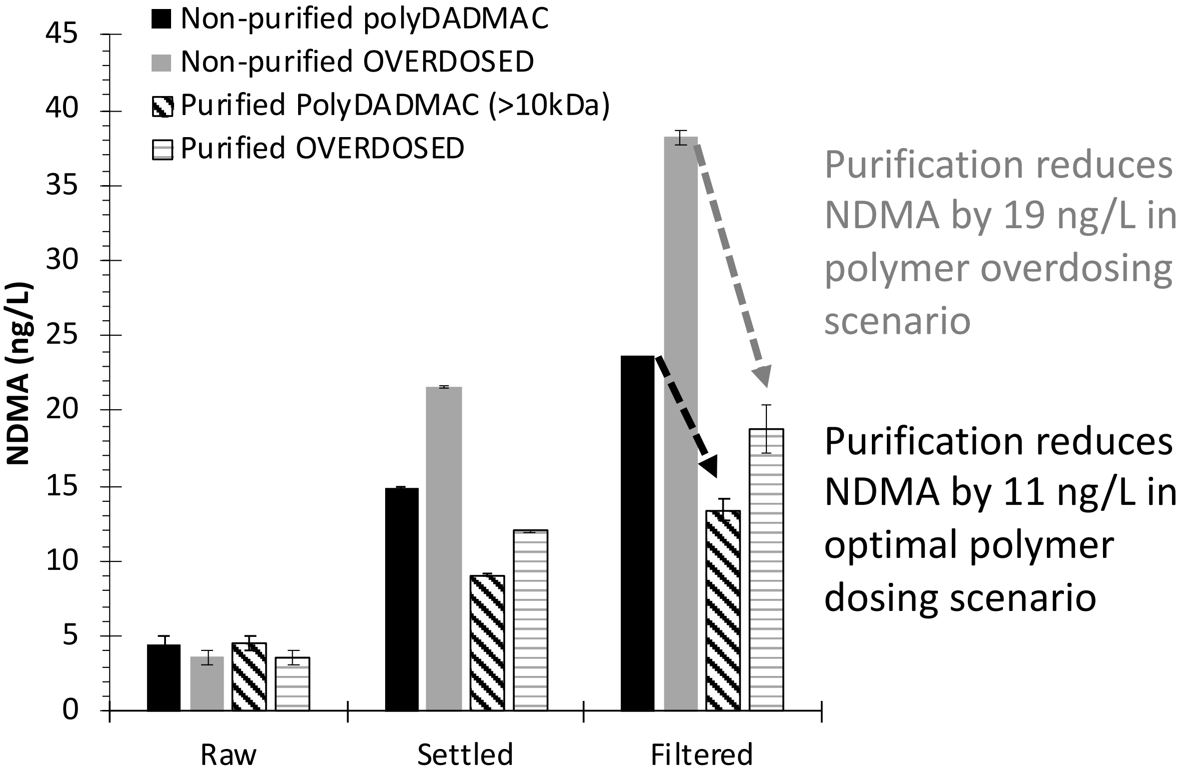

Figure 5 NDMA in the raw, settled, and filtered waters from pilot tests when optimized and overdosed concentrations of non-purified polyDADMAC and purified polyDADMAC (>10 kDa) were used.

Other Methods of Purifying Cationic Polymer Stock Solutions

Diaultrafiltration was selected for the bench- and pilot-scale testing because of its ability to remove polymer residuals based upon molecular weight. However, other purification strategies could be feasible. For example, we considered purging semivolatile compounds from polyDADMAC polymer. While there was no detectable ammonia in the polymer solution, other semivolatile compounds exist, namely DMA. DMA has a Henry's constant of 1.8×10^{-5} atm-m^3/mol. Because the pK_a for DMA is 10.7, we adjusted the pH of the polyDADMAC solution to 10.0 and then evaluated NDMA formation without purging versus after purging for several hours using a porous stone diffuser and an inert gas (N_2). Without N_2 purging, the polyDADMAC solution produced 101±2 ngNDMAFP/mg polymer (168±3 ng NDMAFP/mg DOC). Purging reduced formation to 56±3 ngNDMAFP/mg of polymer (92±5 ng NDMAFP/mg DOC), or a 45% reduction in NDMA ($p<0.05$). These results imply that volatile oligotrophic materials (e.g., DMA and others), likely of low molecular weight (given their volatility), in the non-purified polyDADMAC solution represent a major portion of NDMA precursors. Thus, there may be other ways to purify cationic polymer solutions to reduce their contribution towards NDMA formation at water treatment facilities that use chloramine disinfectants.

Summary and Conclusions

Two major findings were demonstrated in bench-scale jar tests and confirmed in continuous flow pilot-tests. First, cationic polymers contribute to NDMA formation at water treatment plants that utilize chloramine disinfectants. Two source waters with relatively low watershed-precursor NDMA levels were studied, and optimal or overdosing of cationic polymer more than doubled amount of NDMA precursors present in coagulated-settled supernatant waters. This demonstrated that a small portion of non-removable polymer residual was likely contributing to NDMA formation. Mimicking full-scale conditions, pilot testing using raw water containing a chloramine residual showed that NDMA formed during coagulation, where chloramines and polymers were present. Additionally, NDMA formation continued even after sedimentation where both non-removable polymer residuals and chloramines continued to react. These results provide evidence that a portion of polyDADMAC (and polyamine) cationic polymers are reactive in forming NDMA and are not removed during coagulation.

Second, for the first time we show that purifying commercial cationic polymers (polyDADMAC or polyamine) to remove low molecular weight residuals can substantially reduce NDMA precursors in the polymer solutions. Research focused on 10 kDa diaultrafiltration to purify polyDADMAC at the bench- and pilot-scale, but the study also illustrated that even alkaline pH adjustment and purging with an inert gas can be used to purify cationic polymers of NDMA precursors. Diaultrafiltration purification of the cationic polymer did not change its ability to aid in turbidity or DOC removal, but it significantly reduced NDMA formation ($p<0.05$) in settled supernatant water and during pilot-testing using raw water containing chloramine residuals. This work demonstrates the potential for a custom-purified cationic polymer solution, which could be readily manufactured or potentially prepared on-site at water treatment plants, to significantly reduce NDMA formation from cationic polymer-derived precursors.

Conflicts of Interest

There are no conflicts to declare.

Acknowledgements

This research was partially supported by the Water Research Foundation (Project #4622) under the management of Djanette Khari. The authors thank Profs. David Hanigan and Dong An for intellectual input and Laurel Passantino for technical editing.

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