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SM Journal of Public Health and Epidemiology

Research Article

Occurrence, Fate and Preliminary Environmental Risk Assessment of Residual Poly-Diallyldimethyl Ammonium Chloride, and Some Disinfection By-Products, in Treated (Potable), and Environmental, Waters in the Umgeni Water Catchment in Kwazulu-Natal (South Africa)

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Article Information

Received date: Aug 11, 2017
Accepted date: Sep 22, 2017
Published date: Sep 29, 2017

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Keywords Risk assessment; Poly-(Diallyldimethylammonium Chloride); Residual polyelectrolyte; Disinfection By-products; N-Nitrosodimethylamine

Abstract

A preliminary study on the occurrence, fate, and environmental risk assessment of residual Poly-Diallyl Dimethyl Ammonium Chloride (Poly-DADMAC), and some disinfection by-products, in raw dam and treated potable waters, was undertaken. Residual poly-DADMAC in drinking water was determined by the gold nanoparticle, UV-Vis, colorimetric method. The observed, residual poly-DADMAC levels, (range: 1-5µg/L) were, on average (±SD) (µg/L), for the potable water levels, 1.63 (±0.59) for Hazelmere Dam, 1.52 (±0.42) for Midmar Dam, 3.64 (±0.34) for Inanda Dam, and 4.33 (±0.97) for Nagle Dam. The analytical method used to quantify the residual poly-DADMAC was found to be fairly acceptable for the environmental risk assessment of this polymeric coagulant in drinking water. The study indicated compliance of all treated, potable water, for residual poly-DADMAC, to the current international limit of ≤50µg/L. The estimated N-Nitrosodimethylamine (N-NDMA) levels were 142ng/L for Hazelmere and 139ng/L for DV Harris, which exceeded the World Health Organization (WHO) limit of ≤100 ng/L.

Introduction

Poly-Diallyldimethylammonium Chloride (Poly-DADMAC) is an example of a commonly used organic polyelectrolyte, both in wastewater and in potable water treatment plants, as a coagulant and as a flocculent aid, for floc formation and for improved settling of larger particles [1-5]. Due to its potential to form N-Nitrosodimethylamine (N-NDMA) [6-8], there has been, in recent years, a growing concern over the fate of poly-DADMAC within the water treatment process. Some of the early work on N-NDMA has shown it is a disinfection by-product formed during the chlorination steps within the water treatment process [9]. Furthermore, N-NDMA is a suspected carcinogen [1,6,8,10,11].

The presence of residual poly-DADMAC in the final drinking water depends on: its reactivity during the disinfection processes, its degradation into toxic compounds, or other by-products, that pass through the various steps in the water treatment process. Due to the highly charged nature, it is assumed that it will be removed together with the sludge during the flocculation step in the water treatment process. Personal care products are another source of polyelectrolytes that can enter the environment and water treatment plants facilities, where they may not be removed, totally or adequately, during the water treatment process [12,13].

Residual amounts of the polyelectrolyte may persist in the water if the incorrect dose is used. The American Water Works Association, American Society for Testing Materials, The European Committee for Standardization, the National Sanitation Foundation International, and the American National Standards Institute, have provided guidelines for the maximum dosage of polyelectrolytes (10-100 mg/L) that can be used in water treatment. They have limited the residual amount of poly-DADMAC in drinking water at ≤50µg/L [3,14,15]. Recent work has shown that polyelectrolytes, like poly-DADMAC, can be toxic to aquatic-organisms at levels exceeding 50µg/L [12,13].

OPEN ACCESS
ISSN: 2473-0661

Thus, for water treatment plants using poly-DADMAC as coagulant, and from an environmental, human health perspective, there is a strong requirement to determine the amount of residual polyelectrolytes, like poly-DADMAC, in the drinking water. To monitor residual concentrations of the polymer in water, down to the required regulated limit of ≤50μg/L, sensitive, accurate and precise analytical methods are therefore required.

Umgeni Water, a bulk potable water supplier, in KwaZulu-Natal (KZN), makes use of this organic polymeric poly-DADMAC as a coagulant in some of its water treatment plants. We recently reported [16] on the first, novel study regarding residual levels of this polymer in four of Umgeni Waters drinking water plants, using the sensitive spectroscopic technique, which uses citrate-capped gold nanoparticles, developed by Gumbi et al [17]. However, to date the amount of N-NDMA, in the final drinking water from any of the Umgeni Water plants, using poly-DADMAC, has not been fully investigated or accurately determined. Various other Disinfection By-Products (DBPs), like Tri-Halomethanes (THMs) and Dimethylamine (DMA), have also been reported to be present in drinking water [6,18-20].

We hypothesized that there is negligible risk of this residual coagulant (poly-(DADMAC)) to humans from consumption of the drinking water. The aim of this follow-up study was thus: Risk assessment of the residual polymeric coagulant, and some selected disinfection by-products, to humans from consumption of the drinking water produced by Umgeni Water.

This report is now on the environmental risk assessment study of residual polymeric coagulant, and on the levels of some disinfection by-products, in the four Umgeni Water drinking water plants. To our knowledge, this is the first report of: the environmental risk assessment of poly-DADMAC, and some DBPs, in the Umgeni Water catchment waters.

Materials and Methodology

Materials

Sample collection: The four selected raw water sources (dams) (and respective Water Treatment Works (WW)) were: Inanda Dam (Wiggins WW), Nagle Dam (Durban Heights WW), Hazelmere Dam (Hazelmere WW) and Midmar Dam (DV Harris WW). Detailed information has been reported in the previous study [16].

Reagents and chemicals: All chemicals were used without further purification.

Methodology

Instrumentation for poly-DADMAC analysis: Detailed information has been previously reported [16-17]. The UV-Vis, colorimetric, gold-nanoparticle method was used. The Ultraviolet (UV)-Visible (Vis) spectra were measured with an Ocean Optics spectrometer (model HR2000+), equipped with a tungsten halogen (Ocean Optics) based module.

Instrumentation for physical tests: The pH-values of the water samples were measured on site with a Cyberscan portable meter (Hanna HI1230B Gel - filled pH electrodes). Free and total chlorine levels were determined using a Lovibond Chlorine Comparator, the Trihalomethanes (THMs) (chloroform, dichlorobromomethane, chlorodibromomethane, bromo-form) were determined using a Hewlett-Packard GC-ECD, nitrite-nitrate were determined with a Waters ion chromatograph-conductivity detector, and ammonia was determined with an Aquakem discrete auto-analyser. The chloramine was estimated from the observed free and total chlorine levels. The (TOC) was determined using a Tekmar Torch analyser. The Total Dissolved Solids (TDS) were determined by gravimetry at 105±5°C.

Determination of DMA: The DMA levels were estimated using the poly-DADMAC coagulant doses (ranges) for the four water works observed, and the published data [21], which indicated: that cationic polymer solutions contain trace levels of DMA, ranging from 0.21-1.21 μg/mg of active polymer ingredient - i.e., every 1mg/L dose of polymer adds somewhere between 0.21-1.21 μg/L of DMA into the water.

Determination of N-NDMA: A study which investigated the impact of various parameters on N-NDMA formation upon chloramination of organic polymers was reported Najam et al [21], in 2004. The N-NDMA levels in our four drinking water plants were then estimated using their observed data for DMA and N-NMDA [21]. The reported 7- day DMA values, obtained using 1 mg/L poly-DADMAC, (at pH 8.3-8.6; chloramine 3.4-3.6 mg/L, 22°C, 7 day contact time) were first plotted against the corresponding N-NDMA levels (Figure 1). The regression equation we obtained, $y = 77.113x - 108.09$, where y = N-NDMA concentration, and x = DMA concentration, with a correlation coefficient (r^2) = 0.8519, was then used to estimate the N-NDMA in our water samples.

Results

Physico-chemical water quality

The test results are summarized in Table S1. The average values for pH were (mean±SD): 7.82 (±0.17) for Nagle, 7.88 (± 0.16) for Inanda, 8.06 (±0.40) for Hazelmere and 8.49 (±0.31) for Midmar dam. The free and total chlorine levels were: (mean) (±SD) (mg/L) 0.21 (±0.10) and 2.52 (±0.27) for DV Harris, 1.12 (±0.09) and 1.31 (± 0.10) for Durban Heights, 1.16 (±0.15) and 1.36±0.17 for Wiggins, 1.78 (±0.21) and 2.06 (±0.34) for Hazelmere. The nitrite levels were <0.05mg/L for all four water works. The nitrate levels were: 0.22 (±0.02) for DV Harris, 0.25 (±0.02) for Hazelmere, 0.30 (±0.04) for Durban Heights, 0.88 (±0.35) for Wiggins. The ammonia levels (as mg/L N) were: <0.040 for Wiggins and Durban Heights, < 0.04-0.04 for Hazelmere, and 0.672 (0.128) for DV Harris. The TOC levels (mg/L) were: 1.91 (±0.35) for Hazelmere, 2.04 (±0.39) for Midmar, 2.16 (±0.26) for Nagle and 2.33 (±0.27) for Inanda. The TDS levels (mg/L) (±SD) were: 90.4±8.5 for Midmar, 128.5±15.9 for Nagle, 151.4±11.4 for Hazelmere, and 251.2±29.4 for Inanda.

Disinfection by-products

The total THM levels were: (mean) (±SD) (μg/L): 25.1 (±21.6) for Durban Heights, 32.1 (±10.1) for Hazelmere, 38.2 (±20.2) for DV Harris, and 42.5 (±2.3) for Wiggins. The estimated Chloramine levels were: (mg/L): 0.19 for Durban Heights, 0.20 for Wiggins, 0.28 for Hazelmere and 2.31 for DV Harris. The estimated, mean Dimethylamine (DMA) levels were: (μg/L) (range): 0.62 (0.02-1.22) for Wiggins, 1.70 (0.50-2.90) for Durban Heights, 3.20 (0.34-6.06)

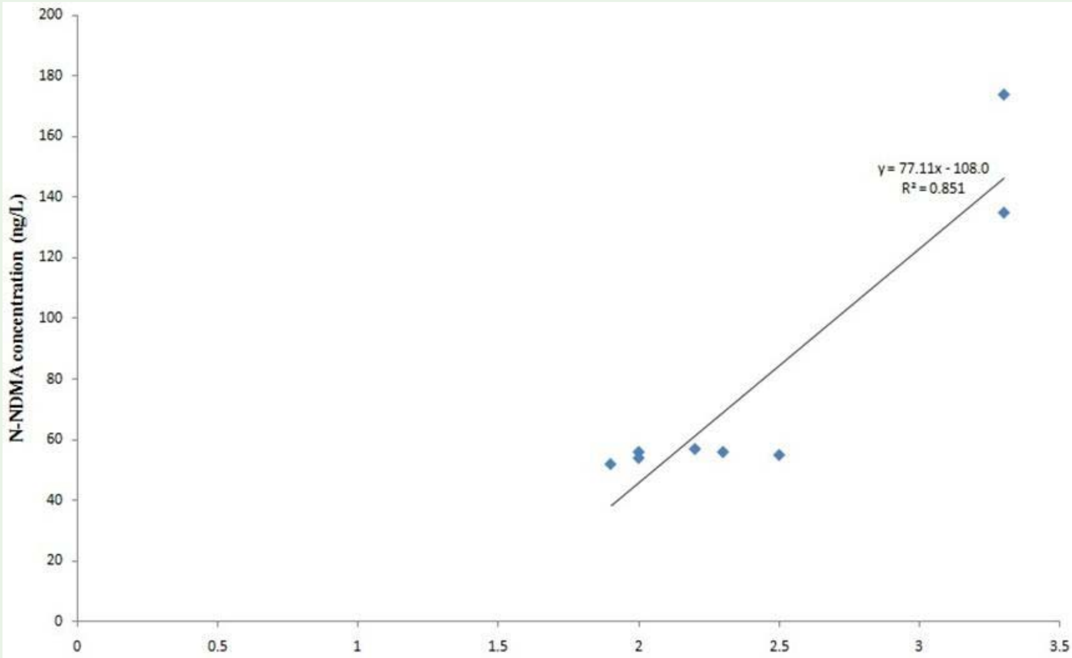

Figure 1: Plot of reported DMA vs. N-NDMA levels.

for DV Harris and 3.24 (0.42-6.06) for Hazelmere. The estimated, N-NDMA levels were: (ng/L): 23 for Durban Heights, 139 for DV Harris, 142 for Hazelmere and -60.3 for Wiggins.

Residual poly-DADMAC levels in the potable water samples

Based on the two values obtained by the test Methods 1 and 2, previously reported [16], the averages for the poly-DADMAC levels for the four potable waters are listed in Table 1: (mean±SD) (µg/L), (% RSD), 1.63±0.59) (36.12) for Hazelmere Dam, 1.52±0.42) (27.91) for Midmar Dam, 3.64±0.34 (9.32) for Inanda Dam, and 4.33±0.97 (22.40) for Nagle Dam.

Table 1: Observed and estimated concentration of disinfection by-products in the drinking waters/potable water works.

Dam/Water works (sample point)	Coagulant dose	Disinfect[b] system	Residual PolyDADMAC (mean±SD) (µg/L)(RSD)	Individual THMs (mean)				Total THMs[b] (±SD) (µg/L) (%RSD)	Nitrite as N (mg/L)	Nitrate as N (mean±SD) (mg/L) (% RSD)	Cl-NH_3[b] (mg/L)	NH_3 as N (Mean±SD) (mg/L) (% RSD)	DMA[b] Mean (range) (µg/L)	*N*-NDMA[b] (ng/L)
				CF (µg/L)	BF (µg/L)	DBCM (µg/L)	BDCM (µg/L)							
Hazelmere/Hazelmere (THM008)	2-5	Chlorine	1.63 ±0.59 -36.12	13.45	≤0.1	8.41	10.23	32.1 (±10.1)[b] -31.46	<0.05	0.25 ±0.02 (8.00	0.28	<0.040-0.040	3.24 (0.42-6.06)	142
Midmar/DV Harris (TMM007)	1.63-5	Chlor = Amination	1.52 ±0.42 -27.91	≤0.3	≤0.1	≤0.1	≤0.06	38.2 (±20.2) -52.88	<0.05	0.22 ±0.02 9.09	2.31	0.672 ±0.128 -19.05	3.2 (0.34-6.06)	139
Inanda/Wiggins (TWG010)	0.08-1.01	Chlorine	3.64 ±0.34 -9.32	≤0.3	≤0.1	≤0.1	≤0.06	42.5 (±2.3) -5.41	<0.05	0.88 ±0.35 39.77	0.2	<0.040	0.62 (0.02-1.22)	(-60.3)
Nagle/Durban Heights (TDH010)	2.4	Chlorine	4.33 ±0.97 -22.4	≤0.3	≤0.1	≤0.1	≤0.06	25.1 (±21.6) -86.06	<0.05	0.3 ±0.04 13.33	0.19	<0.040	1.7 (0.50-2.90)	23
Regulatory limits														
SANS 241-1: 2015, Edition 2			-	≤300	≤100	≤100	≤60	≤1[j]	≤0.9	≤11	≤3	≤1.5 mg/L	-	-
WHO			- 50	≤0.3	≤0.1	≤0.1	≤0.06		0.2 (long-term) 3 (short-term)	50mg/L	3	≤35 (taste) ≤1.5 (odor)		100

[a] Poly-(DADMAC)

[b]Disinfect = Disinfection; THM = Trihalomethanes (individual THMS in brackets: CF = Chloroform; BF = Bromoform; DBCM = Dibromochloromethane; BDCM = Bromodichloromethane)); Cl-NH_3 = Chloramine; DMA = Dimethlyamine; NMDA = N-Nitrosodimethylamine

[c] Cl_2:NH_3= 1.94

from polymer

from y = 77.113x - 108.09

[j]The sum of the ratios of the concentrations of each to its respective guideline value should not exceed 1.

There is minimal difference in pH, which ranges from 6.8 for Inanda, to 7.2 for Midmar. These values do comply with the South African National Standards (SANS 241: 2015-1) [22] for drinking water quality limit of ≥5 to ≤9.7. The average Total Organic Carbon (TOC) levels increase in the order: Nagle < Hazelmere < Inanda < Midmar. However, levels for all for dams comply with the SANS 241-1: 2015 limit of ≤10mg/L.

Discussion

Toxicity, occurrence fate and risk assessment of poly-DADMAC and some disinfection by-products in drinking water from the Umgeni Water catchments

Regulatory limits and toxicity: There is currently no permissible, or stipulated limits on the residual amount of poly-(DADMAC) in drinking water, by the major international regulatory water authorities, like the WHO, US EPA and AWWA. However, there are only two references [23,24], which refer to a regulated residual concentration in drinking water, of 50μg/L, in the USA. There is currently very little toxicity studies on the polymer, poly-(DADMAC). One study, in 2008, reported an EC 50 of 0.5mg/L (500μg/L) for poly-(DADMAC), by using fish immobilisation studies with *Gambusia holbrooki* [13].

Occurrence of poly-DADMAC: The current study has indicated drinking water levels of residual poly-DADMAC of: (mean±SD) (μg/L), 1.21 (±1.31) for Hazelmere Dam, 1.22 (±0.55) for Midmar Dam, 3.40 (±3.89) for Inanda Dam, and 3.64 (±3.83) for Nagle Dam, by Method 1. The overall mean value (±SD) is 2.37μg/L (±1.33) (range: < 2-8 μg/L).

Fate of added poly-DADMAC in the water treatment process: Polyelectrolyte applications in potable water production and industrial waste water treatment are in the coagulation and flocculation steps, and dewatering of treatment plant sludge. Polyelectrolytes have a strong tendency to adsorb onto surface of particles in aqueous suspension, and this is the main reason why they are widely used in water treatment processes. The water industries are responsible for producing safe drinking water for people and all organisms in rivers, lakes and oceans. To keep water safe, polyelectrolytes are required to mix with turbid natural water for removing solid waste material before filtration.

The main aim of introducing polyelectrolytes in water treatment is to induce flocculation and coagulation processes for the removal of suspended solid particles (colloidal matter). All waters, especially surface water, contain both dissolved and suspended particles, which are often assumed to be negatively charged. In suspension particles repel each other and they cannot come together (stay stable in solution). As a result, they will remain in suspension. Coagulation is the process where polyelectrolytes are added to destabilize the suspension or affect the surface of water. In coagulation, polyelectrolytes, overcome the factors that keep particles apart such as repulsion forces, and enable the particles to come together to form micro-flocs (flocs are cluster of small particles).

In the flocculation process, polyelectrolytes are further added to induce the agglomeration of micro-flocs to form macroflocs (bigger particles). The macro-flocs, containing poly-DADMAC, settle or precipitate out of water, and are removed as sludge.

In the four water works studied, the polymeric coagulant dose, added to raw dam water, ranged from 1-5.2 mg/L (1,000-5,200 μg/L), and the residual poly-DADMAC levels observed in the treated drinking waters was, on average, 2.37μg/L (0.05-0.24%), compliant with the international limit of ≤50μg/L.

Disinfection systems: Chlorine (gas) is used as a disinfectant for the three waterworks: Hazelmere, Wiggins, Durban Heights, while chloramine (chlorine gas/liquid ammonium hydroxide (25% m/m ammonia)) is used at the DV Harris waterworks. None of the studied waterworks currently use ozone for disinfection of the treated water.

Precursors of nitrogenous disinfection by-products in drinking water: Disinfection of drinking water using chlorine has delivered major public health improvements worldwide by suppressing waterborne diseases. However, the downside to chlorination is the formation of hazardous Disinfection By-Products (DBPs) through reactions between precursor materials and disinfectants, mainly chlorine, but also chloramines, ozone, chlorine dioxide and UV disinfection.

As a result, various studies have been reported on the precursors and the occurrence of the various DBPs in drinking water [25-27]. Additionally, there have been many similar reports on the specific DBP, N-Nitrosodimethylamine (N-NDMA), from the precursor's polyamine, and poly-DADMAC [28-34].

With the initial discovery that reactions between organic matter and chlorine in drinking water were responsible for production of chlorine (Trichloromethane) (TCM) (Trihalomethane) (THM), the US EPA regulated levels of THMs in drinking water at 100μg/L. Subsequently, the following compounds were found and quantified in drinking water: Haloacetic Acids (HAAs), Di-Haloacetonitriles, Haloketones, Chloral Hydrate, Cyanogen Chloride, Chloropicrin and Haloacetamides. The THMs, followed by the HAAs, were the largest groups present on a mass basis, with summed N-DBP groups, typically present at under 10μg/L.

Chloramines have been found to promote cyanogen chloride and N-NDMA formation; ozonation before chlorination increases chloropicrin and even medium pressure UV disinfection prior to chlorination has been reported to slightly enhance the halonitromethane formation.

Mammalian cell tests have shown that the haloacetonitriles, halonitromethanes and haloacetamides are all far more cytotoxic and genotoxic than the THMs and HAAs, although the haloacetaldehydes also present very high toxicity.

N-Nitrosodimethylamine (N-NDMA)**:** In 2002, N-Nitrosodimethylamine (N-NDMA) was formally recognized as a DBP resulting from monochloramination of dimethylamine.

The N-nitrosamines constitute an emerging group of disinfection by-products that exhibit unusually high carcinogenic risk (10^{-6} cancer risk level at concentration as low as 0.7ng/L for N-NDMA). However these compounds are frequently detected in treated drinking waters and wastewater at levels higher than their advisory guidelines in the United States and other parts of the world. Of all the nitrosamines, N-NDMA has been most commonly detected, with concentrations ranging from 0-630 ng/L, with an average of 9ng/L in treated drinking waters and up to 1000ng/L in wastewater effluents. Recent N-NDMA occurrence data showed the presence of N-NDMA above the method reporting limit of 2ng/L at nearly 25% of public water utilities screened for nitrosamines.

Past studies on N-NMDA formation mechanisms have shown Dimethylamine (DMA) as a precursor for N-NDMA. However DMA alone cannot account for the entire mass of N-NDMA formed. Hence, efforts to identify other potential N-NDMA precursors and formation pathways are critical to develop proper strategies to minimize N-NDMA formation during water and wastewater treatment.

The international regulation guidelines for N-NDMA (Maximum Concentration Limit (MCL) (ng/L)) in drinking water ranges from 0.7-100 ng/L, as follows: US EPA: 0.7 [35], Guidelines for Canadian Drinking Water Quality: 40 [36], California Department of Public Health: 3 [36], UK Guidelines: ± 9-10 [37], Australian National Health and Medical Research Council: 100 [38], and the World Health Organization: 100 [39].

To date it is estimated that 600-700 DBPs have been reported from the use of chlorine, ozone, chlorine dioxide, and chloramines.

Observed and estimated DBPs in the Umgeni Water drinking water sites

THMs: The national South African SANS 241-1: 2015 drinking water quality guide [22] stipulates the following limits: ≤300µg/L for chloroform, ≤100µg/L for bromoform, ≤100µg/L dibromochloromethane, ≤60µg/L bromodichloromethane, with an additional Combined Ratio of ≤1. The international WHO [41-42] limits are the same: ≤300µg/L for chloroform, ≤100µg/L for bromoform, ≤100µg/L dibromochloromethane, ≤60µg/L bromodichloromethane, with an additional Combined Ratio of ≤1.

Nitrite and nitrate: The national South African SANS 241-1: 2015 drinking water quality guide [22] stipulates the following limits: ≤0.9mg/L for nitrite, and ≤11mg/L for nitrate. The international WHO [40-41] limits are 0.2mg/L (short term), 3mg/L (long term) for nitrite, and 50mg/L for nitrate.

Monochloramine: The monochloramine levels for the drinking water from the four water works were estimated from the difference between the corresponding total and free chlorine levels. The national South African SANS 241-1: 2015 [22] drinking water quality guide stipulates ≤3mg/L as the limit. The international WHO limit is 3mg/L. The estimated levels ranged from 0.28mg/L (Hazelmere) to 2.31mg/L (DV Harris). Thus all 4 water works comply with the national and international limits of ≤3 mg/L.

DMA: The DMA levels were estimated using the poly-DADMAC coagulant doses (ranges) for the four water works observed, and the published data, which indicated: that cationic polymer solutions contain trace levels of DMA, ranging from 0.21µg/mg-1.21µg/mg of

Table 2: Various N-NDMA reported guideline/regulatory concentrations in drinking water.

No.	Date/ Year	Document Reference/Title	Description of the Limits/guides	Concentration (ng/L)
1	2009	US EPA EPA 505-F-09-008	0.7ng/L: Ground water	0.7
			0.42ng/L: EPA Regions 3 and 6	0.42
			3ng/L: California	3
2		Integrated Risk Information System (IRIS) Chemical Assessment Summary, US EPA, National Centre for Environmental Assessment	Drinking water unit risk: 1.4x10^{-3}µg/L	0.14
3	2000	Ontario Ministry of the Environment and Energy	Maximum Acceptable Concentration 9ng/L	9
4	2002	California Dept of Health (DHS)	Interim action level 10ng/L	10
5	2013	OEHHA, California, Health Risk Information for Public Health Goal Exceedance	Public Health Goal 0.000003mg/L (3ng/L)	3
6	2006	Public Health Goals (PHG) for Chemicals in Drinking Water, N-Nitrosodimethylamine, 2006	PHG 0.003ppb	3
7	2006, 2008	*N*-Nitrosodimethylamine in drinking water. Background document for development of WHO *Guidelines for Drinking-water Quality. WHO/HSE/AMR/08.03/8, WHO 2008*	Guideline Value (HBV/health-based value) for drinking water 100ng/L	100
8	2014	EPA United States Environmental Protection Agency. Technical Fact Sheet - N-Nitroso-Dimethylamine (N-NDMA)	Drinking water unit risk: 1.4x10^{-3}µg/L	0.14
			1x10^{-6} Cancer risk level: 0.7 ng/L	0.7
			Included on 3rd CCL3	
			Contaminant Candidate List	
			Preliminary remediation goal in groundwater: 1.3ng/L	
			Tap water screening level (1x10^{-6} Cancer risk level): 0.42ng/L	0.42
9	2011	Guidelines for Canadian Drinking Water Quality. Guideline Technical Document. N-Nitroso-Dimethylamine (N-NDMA), Federal-Provincial-Territorial Committee on Drinking Water, Ontario	Maximum Acceptable Concentration for drinking water: 0.04µg/L	40
10	2016	EPA United States Environmental Protection Agency. Chemical Contaminants - CCL 4, Final CCL 4 Chemical Contaminants	Known to occur in public water systems: N-NDMA (CASRN: 62-75-9)	
		Computed Mean		**15.19**
		Computed SD		**30.43**
		Computed Range		**0.14-100 ng/L**

active polymer ingredient - i.e., every 1mg/L dose of polymer adds somewhere between 0.21µg/L-1.21µg/L of DMA into the water [30]. Using the latter as a guide, the DMA levels were estimated, and increased in the following order (µg/L):

Wiggins (0.62) < Durban Heights (1.70) < DV Harris (3.20) < Hazelmere (3.24), in proportion to the coagulant poly-DADMAC dose. The national South African SANS 241-1: 2015 drinking water quality guide [22], and the WHO, does not include a limit for DMA.

N-NDMA

Regulatory guidelines: The international regulation guidelines for N-NDMA (Maximum Concentration Limit (MCL) (ng/L)) in drinking water ranges from 0.14-100 ng/L (Table 2): US EPA: 7, and the World Health Organisation: 100.

There is currently no stipulated guide for N-NDMA in the national South African drinking water quality guide: SANS 241-1: 2015. The N-NDMA levels in the four drinking water plants were estimated using the reported, observed data and the derived regression equation: N-NDMA = y = 77.113*x* -108.09. Using this equation, our estimated values for N-NDMA indicate levels above the international limits of 7ng/L (US EPA), and 100ng/L (WHO), for drinking water from two water works: Hazelmere (142ng/L) and DV Harris Water Works (139ng/L).

The formation of N-NDMA can also occur in the absence of ammonia by the nitrosation pathway [9,42]. The reaction of HOCl with nitrite forms, as intermediates, a Dinitrogen Tetroxide (N_2O_4), which is favored at neutral pH, or a di-Nitrogen Trioxide (N_2O_3) at low pH. The formation of N-NDMA is made possible by the reaction of these intermediates on DMA. Maximum N-NDMA formation is observed between pH 6 and 8 [43]. The pH-values on the drinking water sites in this study range from 7.8 to 8.5. However, the highest N-NDMA estimated levels are for those waterworks with pH 8.06 (142ng/L for Hazelmere) and 8.49 (139 ng/L for DV Harris), which are slightly above pH 8.

Previous studies on N-NMDA levels in South African waters: The literature indicates only 3 reports [44-46] with no quantitative data on actual concentrations being measured. N-NDMA was detected, but not quantitated, by GC-MS, at the Balkfontein water treatment plant, as a DBP of mono-chloramine since the plant used chloramination as a disinfectant step [44].

Conclusion

The estimated levels of N-NDMA indicate levels above the international WHO limit of ≤100ng/L for drinking water from the two water works: Hazelmere and DV Harris. Based on the high carcinogenic risk (10^{-6} cancer risk level at concentration as low as 0.7ng/L for N-NDMA), these levels imply risk to cancer from ingestion of the drinking water.

Future research work must consider, *inter alia*, the actual measurement of DMA and N-NDMA in the drinking water from all four potable water works that use poly-DADMAC as coagulant in the water treatment process, and investigation of water treatment processes to remove or minimize any observed levels of N-NDMA to acceptably safe levels.

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