Science of the Total Environment 520 (2015) 120–126

Contents lists available at ScienceDirect

Science of the Total Environment

journal homepage: www.elsevier.com/locate/scitotenv

Seasonal and spatial variability of nitrosamines and their precursor sources at a large-scale urban drinking water system

Gwen C. Woods [a], Rebecca A. Trenholm [a], Bruce Hale [b], Zeke Campbell [b], Eric R.V. Dickenson [a,*]

[a] Southern Nevada Water Authority, P.O. Box 99954, Las Vegas, NV 89193-9954, USA
[b] Denver Water, 1600 West 12th Avenue, Denver, CO 80204-3412, USA

HIGHLIGHTS

- Nitrosamines were examined in a drinking water system utilizing chloramines.
- Only *N*-nitrosodimethylamine (NDMA) was detected throughout the system.
- Seasonal variations indicate that greater NDMA forms in cooler temperatures.
- Evidence is provided that NDMA sources may originate from the distribution system.
- Results provide insight into NDMA linked to changes in water quality.

ARTICLE INFO

Article history:
Received 9 January 2015
Received in revised form 2 March 2015
Accepted 3 March 2015
Available online 22 March 2015

Editor: D. Barcelo

Keywords:
N-nitrosodimethylamine
Full-scale
Distribution system
Seasonality
Disinfection by-products
Occurrence

ABSTRACT

Nitrosamines are considered to pose greater health risks than currently regulated DBPs and are subsequently listed as a priority pollutant by the EPA, with potential for future regulation. Denver Water, as part of the EPA's Unregulated Contaminant Monitoring Rule 2 (UCMR2) monitoring campaign, found detectable levels of *N*-nitrosodimethylamine (NDMA) at all sites of maximum residency within the distribution system. To better understand the occurrence of nitrosamines and nitrosamine precursors, Denver Water undertook a comprehensive year-long monitoring campaign. Samples were taken every two weeks to monitor for NDMA in the distribution system, and quarterly sampling events further examined 9 nitrosamines and nitrosamine precursors throughout the treatment and distribution systems. NDMA levels within the distribution system were typically low (>1.3 to 7.2 ng/L) with a remote distribution site (frequently >200 h of residency) experiencing the highest concentrations found. Eight other nitrosamines (*N*-nitrosomethylethylamine, *N*-nitrosodiethylamine, *N*-nitroso-di-n-propylamine, *N*-nitroso-di-n-butylamine, *N*-nitroso-di-phenylamine, *N*-nitrosopyrrolidine, *N*-nitrosopiperidine, *N*-nitrosomorpholine) were also monitored but none of these 8, or precursors of these 8 [as estimated with formation potential (FP) tests], were detected anywhere in raw, partially-treated or distribution samples. Throughout the year, there was evidence that seasonality may impact NDMA formation, such that lower temperatures (~5–10 °C) produced greater NDMA than during warmer months. The year of sampling further provided evidence that water quality and weather events may impact NDMA precursor loads. Precursor loading estimates demonstrated that NDMA precursors increased during treatment (potentially from cationic polymer coagulant aids). The precursor analysis also provided evidence that precursors may have increased further within the distribution system itself. This comprehensive study of a large-scale drinking water system provides insight into the variability of NDMA occurrence in a chloraminated system, which may be impacted by seasonality, water quality changes and/or the varied origins of NDMA precursors within a given system.

1. Introduction

With the advent of the EPA's Stage 2 DBP rule, treatment facilities have increasingly converted from chlorine to chloramine disinfection to reduce regulated disinfection by-products (DBPs), namely trihalomethanes (THMs) and haloacetic acids (HAAs). Nitrosamines are a class of unregulated DBPs that are prevalent with the use of chloramines (Krasner et al., 2013), are probable human carcinogens (USEPA, 1991), and are perceived to pose a greater health risk than currently regulated DBPs (Shah and Mitch, 2012). Five nitrosamine species are acknowledged by the EPA's third Contaminant Candidate List (CCL-3) (USEPA, 2009), six are listed in the second Unregulated Contaminant Monitoring Rule 2 (UCMR2) (USEPA, 2012), and future EPA regulation of nitrosamines is a possibility. Among the most widely identified and

* Corresponding author.
E-mail addresses: gwen.woods@utoronto.ca (G.C. Woods), eric.dickenson@snwa.com (E.R.V. Dickenson).

http://dx.doi.org/10.1016/j.scitotenv.2015.03.012
0048-9697/

monitored nitrosamines is *N*-nitrosodimethylamine (NDMA), a nitrosamine species found above the minimum reporting level in ~50% of samples in treatment systems utilizing chloramination as a primary disinfectant (UCMR2 database) (Woods and Dickenson, 2015; USEPA, 2012). The USEPA estimates that NDMA has a 10^{-6} cancer risk level of 0.7 ng/L in drinking water (USEPA, 1993). The US Office of Environmental Health Hazard Assessment has issued a health goal of 3 ng/L (CDPH, 2013), while Ontario (Canada) has a standard of 9 ng/L. Australia regulates NDMA at 10 ng/L (QPC, 2005), and the World Health Organization has issued a 100 ng/L guideline (WHO, 2008).

It is becoming increasingly apparent in the water industry that no single disinfection technique is free from DBP formation, and that further research is necessary to better understand both the reduction of DBP formation and subsequent trade-offs necessary to keep all species minimized. Widespread occurrence data of nitrosamines, however, are still somewhat lacking, particularly studies that have examined temporal variability. Of studies that have been conducted, a survey of 36 drinking water systems in California found NDMA associated with ion exchange treatment as well as recycled water (CDPH, 2002). Quarterly data from 21 drinking water systems in the USA and Canada, likewise found that chloraminated systems produced more NDMA, and that levels were generally higher in distribution systems. This study did not discuss seasonal variability (Barrett et al., 2003). Other surveys include the examination of 38 drinking water systems in North America, wherein distribution samples were also found to contain elevated NDMA concentrations (Boyd et al., 2011), and a comprehensive study in Ontario, Canada from 1998 to 2009 (MOE, 2013). Data from 1998 to 2007 from the Ontario survey was examined previously (Russell et al., 2012), but information such as disinfectant use was not reported, and seasonality was not discussed. Finally, the USEPA's UCMR2 survey is spatially the most comprehensive survey to-date, with some 1199 utilities required to monitor for nitrosamines on a bi-yearly (groundwater) or quarterly (surface water) basis. Variability across regions is apparent from this dataset, but may, to some extent, be a product of regional differences in disinfection practices; seasonality was overall found to have no clear trend with NDMA occurrence (Woods and Dickenson, 2015). While important information is gleaned from the above-mentioned occurrence studies, more comprehensive analyses of individual water systems may render useful information such as regional variability with climate, detailed information about plant practices, and testing for nitrosamine precursors so as to better define the origins of precursors. The research presented here sought to capture a thorough investigation of nitrosamine occurrence at a full-scale urban drinking water treatment facility, and examine detailed occurrence both spatially and temporally.

Characterization of nitrosamine precursors may enable utilities to manage source water supplies and treatment practices to minimize nitrosamine formation. Heavy loadings of NDMA precursors in utility source waters have been linked to wastewater-impact (Krasner et al., 2008; Schmidt and Brauch, 2008; Nawrocki and Andrzejewski, 2011; Shen and Andrews, 2011; Russell et al., 2012). Earlier research proposed that secondary amines present in wastewater or other natural waters may form a hydrazine intermediate which further reacts with monochloramines to form NDMA (Choi and Valentine, 2002; Mitch and Sedlak, 2002). Other research has sought to address inputs of natural sources of NDMA precursors into raw water, but naturally-derived precursors appear to have lower NDMA yields than many of the anthropogenically-derived compounds tested (Dotson et al., 2009; Gerecke and Sedlak, 2003; Krasner et al., 2013). Materials from within the water treatment process may contribute significant NDMA precursors. In plants utilizing anion exchange treatment, resins with tertiary and quaternary amine functional groups contain NDMA precursors that may be released during treatment (Flowers and Singer, 2013; Kemper et al., 2009; Nawrocki and Andrzejewski, 2011). Recent research further highlights nitrosamine formation from organic polymer aids following oxidation with chlorination or chloramination (Kemper et al., 2010; Mitch and Sedlak, 2004; Park et al., 2009a,b; Wilczak et al., 2003). Coagulant polymer aids that contain quaternary ammonium cations, such as epichlorohydrin (Park et al., 2009a,b) and the widely-used polyDADMAC (Najm and Trussell, 2001; Park et al., 2009a,b; Wilczak et al., 2003), have been identified as high-yielding NDMA precursors. Finally, origins from distribution system materials, such as rubber gaskets and seals have been identified (Morran et al., 2011; Teefy et al., 2011), although relatively little research has been designated to distribution precursors.

As part of the USEPA's second Unregulated Contaminant Monitoring Rule (UCMR2), all public water systems serving >100,000 people were required to monitor for six nitrosamines, including NDMA (Table 1). The urban public drinking water system, Denver Water, serves some 1.2 million people (Denver Water, 2014) and was included in this survey. Denver Water's water supply originates primarily from mountain snowmelt. Anthropogenic impacts such as wastewater influence are considered low, but the treatment plants do utilize the coagulant polymer aid polyDADMAC as well as chloramines for final disinfection. The quarterly UCMR2 results from three sites of maximum residency in the distribution system resulted in detectable levels of NDMA (≥2 ng/L) in all but 2 of the 12 samples, with values ranging from 2.0 to 4.7 ng/L (median value of 2.8 ng/L); 3 entry point sampling sites resulted in no detection of NDMA on any of the sampling dates. The other five nitrosamines included in the UCMR2 survey were not found at detectable levels. Following discovery of NDMA in distribution samples, Denver Water in collaboration with the Southern Nevada Water Authority initiated a more intensive monitoring survey to better understand the temporal and spatial variability of nitrosamines, as well as nitrosamine precursors. Biweekly sampling was conducted throughout 2013 at points of maximum residency in the distribution system (UCMR3 sites) as well as more extensive sampling campaigns conducted on a quarterly basis with samples from source waters and partially treated waters. During the quarterly sampling, 8 other nitrosamines of concern were measured (Table 1) and formation potential (FP) tests were performed to estimate nitrosamine precursor loadings throughout the treatment and distribution systems. To the best of our knowledge, this is the most temporally-intensive sampling campaign ever conducted for nitrosamines in a full-scale system. The results lend insight into seasonal effects on NDMA formation as well as evidence of NDMA precursors originating from within the distribution system, a category of precursors much less studied than source water precursors.

Table 1
Suite of 9 nitrosamines analyzed quarterly at Denver Water (Dec. 2012–Dec. 2013).

Nitrosamine species	Cancer risk level (ng/L)	Included in CCL3	Included in UCMR2	MRL from UCMR2 (ng/L)	MRL from this study (ng/L)
N-nitrosodimethylamine (NDMA)	0.7	x	x	2	1.3
N-nitrosomethylethylamine (NMEA)	2		x	3	2.5
N-nitrosodiethylamine (NDEA)	0.2	x	x	5	5.0
N-nitroso-di-n-propylamine (NDPA)	5	x	x	7	10
N-nitroso-di-n-butylamine (NDBA)	6		x	4	10
N-nitroso-di-phenylamine (NDPhA)	7000	x			10
N-nitrosopyrrolidine (NPYR)	16	x	x	2	10
N-nitrosopiperidine (NPIP)	0.8				5.0
N-nitrosomorpholine (NMOR)	0.8				5.0