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Seasonal and temporal patterns of NDMA formation potentials in surface waters

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ARTICLE INFO

Article history:
Received 15 July 2014
Received in revised form
12 November 2014
Accepted 13 November 2014
Available online 21 November 2014

Keywords:
NDMA formation potential (FP)
Seasonal and temporal patterns
Precipitation
Nitrosamines
Wastewater influence
Sucralose

ABSTRACT

The seasonal and temporal patterns of *N*-nitrosodimethylamine (NDMA) formation potentials (FPs) were examined with water samples collected monthly for 21 month period in 12 surface waters. This long term study allowed monitoring the patterns of NDMA FPs under dynamic weather conditions (e.g., rainy and dry periods) covering several seasons. Anthropogenically impacted waters which were determined by high sucralose levels (>100 ng/L) had higher NDMA FPs than limited impacted sources (<100 ng/L). In most sources, NDMA FP showed more variability in spring months, while seasonal mean values remained relatively consistent. The study also showed that watershed characteristics played an important role in the seasonal and temporal patterns. In the two dam-controlled river systems (SW A and G), the NDMA FP levels at the downstream sampling locations were controlled by the NDMA levels in the dams independent of either the increases in discharge rates due to water releases from the dams prior to or during the heavy rain events or intermittent high NDMA FP levels observed at the upstream of dams. The large reservoirs and impoundments on rivers examined in this study appeared serving as an equalization basin for NDMA precursors. On the other hand, in a river without an upstream reservoir (SW E), the NDMA levels were influenced by the ratio of an upstream wastewater treatment plant (WWTP) effluent discharge to the river discharge rate. The impact of WWTP effluent decreased during the high river flow periods due to rain events. Linear regression with independent variables DOC, DON, and sucralose yielded poor correlations with NDMA FP ($R^2 < 0.27$). Multiple linear regression analysis using DOC and log [sucralose] yielded a better correlation with NDMA FP ($R^2 = 0.53$).

1. Introduction

An increasing number of drinking water utilities in the United States (US) have been employing or considering chloramination for disinfection to comply with the stringent regulations for trihalomethanes (THMs) and haloacetic acids (HAAs). However, nitrosamines, a class of emerging disinfection by-products (DBPs), may occur in chloraminated waters (Choi and Valentine, 2002a,b; Mitch et al., 2003). As a result, there has been an increased regulatory attention by the US Environmental Protection Agency (EPA) that included nitrosamines in the Contaminant Candidate List 3 (CCL3). Nitrosamines are classified as probable human carcinogens in

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http://dx.doi.org/10.1016/j.watres.2014.11.017
0043-1354/

water at very low concentrations; for instance, with a 10^{-6} lifetime cancer risk for 0.7 ng/L of *N*-nitrosodimethylamine (NDMA) in drinking water (USEPA, 2002). NDMA is the most commonly detected and reported nitrosamine in distribution systems in the US (Russell et al., 2012).

Considering possible future regulations, several US drinking water utilities have developed a strong interest in understanding the formation and control of NDMA in their systems. In order to better manage the water sources and treatment operations, the impacts of various temporal and climatic events (e.g., drought periods, spring run offs or major rains, algae growth/die off, seasonal effects, and lake turnovers) on the seasonal changes in the occurrences of NDMA precursors in source waters need to be understood. However, there are only a few studies with limited focus and sampling events on the temporal variations of the NDMA and other nitrosamines precursors in natural waters. While studying the contributions of wastewater effluents to DBP formation, Krasner et al. (2008) investigated the formation potentials (FPs) of several classes of carbonaceous DBPs and nitrosamines in water samples collected from the South Platte River watershed area in February and September, 2004 and April, 2005. Observed NDMA FP tended to increase with increasing dissolved organic nitrogen (DON), however, the correlation between NDMA FP and DON was not strong. Mitch et al. (2009) investigated 11 water treatment plants and their associated source waters in the summer and fall of 2006 (each plant was sampled once) for occurrence of several carbonaceous DBPs and nitrogenous DBPs as well as their precursors. To evaluate year-to-year variability, a follow-up survey was conducted in 2007 (spring, summer, and fall) for these 11 sites plus 5 other plants. Their sampling strategy was designed to demonstrate the impact of wastewater effluents and algal bloom events. Thus, water samples rich in DON contents were obtained and analyzed. No correlation was found between NDMA FP and DON, which is similar to the results obtained by Krasner et al. (2008), even though different water samples from different sources were examined. Mitch et al. (2009) hypothesized that DON contributions from algae and other sources would confound any association between DON and NDMA FP. Amino acids are an important component of DON, but no significant correlation was observed between total amino acids and dissolve organic carbon (DOC) or DON, suggesting that DON composition is site-specific. A few more studies have investigated seasonal effects on the NDMA precursors and evaluated possible relationships between NDMA precursors and water quality parameters (Zhang et al., 2014; Aydin et al., 2012; Valentine et al., 2006). However, seasonal patterns of NDMA precursors were not scrutinized thoroughly and no strong correlations between NDMA FP and other factors due to insufficient sample collection for limited time periods.

Although previous research has provided some useful information on the NDMA precursors in source waters, comprehensive studies detailing the effect of dynamic events in watersheds on the occurrence and reactivity of NDMA and other nitrosamine precursors are lacking in the literature. Therefore, main objectives of this study were to (i) monitor NDMA precursors' levels by measuring NDMA FPs in various surface waters, (ii) investigate the impacts of seasonal variations and climatic events on the NDMA FP with a comprehensive long term study, and (iii) examine correlations between NDMA FP with selected water quality parameters. Water samples were collected from 12 surface waters which are currently used as source waters by 9 drinking water treatment plants during the period of 2012–2014. The source waters included rivers, lakes, and reservoirs located on different watersheds. The FP tests (i.e., chloramination for NDMA and chlorination for THM) were conducted to measure NDMA and THM precursor levels in collected water samples and the occurrence of NDMA and THM were also monitored. THM FP was included in the study due to its current regulatory importance in the US and for the purpose of comparison. To the best of our knowledge, this is currently the longest monitoring study in the literature on NDMA FP and THM FP in selected source waters.

2. Materials and methods

2.1. Sampling and FP test

Water samples were collected (on a monthly basis for February 2012–August 2013 and then quarterly until February 2014) from 12 different source waters (3 rivers and 9 lakes/reservoirs) located in the Southeastern United States. Most of the sampling sites were located near or at the intakes of drinking water treatments plants. For the occurrence of NDMA in the source waters, samples collected in 1000 mL amber bottles were quenched immediately with sodium thiosulfate (~30 mg), transferred to the laboratory, and stored at 4 °C until analysis. To determine NDMA precursor levels, water samples were collected for the FP tests in 1000 mL amber glass bottles, and brought to the laboratory where phosphate buffer (20 mM) was added to each bottle to maintain pH at 7.8. Then, pre-determined volume of monochloramine (Cl:N = 4:1) stock solution was spiked in the bottles to achieve 100 mg/L of monochloramine. Each bottle was filled headspace free with a sample. After 5 days of contact time at room temperature in the dark, samples were quenched with sodium thiosulfate, extracted, and analyzed using GC/MS/MS. For the purpose of comparison, the occurrence and FP of THM were also measured with concurrently collected samples. For the occurrence of THM, sodium sulfite was added as a quenching agent. THM FP tests were conducted in the presence of 50 mg/L of chlorine at pH 7.8 for 5 days contact time, and then THM samples were extracted and analyzed using GC/ECD.

2.2. Analytical methods

NDMA and other nitrosamines were analyzed following USEPA method 521 (USEPA, 2004) using Varian GC 3800-MS/MS 4000 under CI mode equipped with RTX-5MS (Restek 30 m × 0.25 mm × 0.25 μm) capillary column. THMs were measured following USEPA Method 551.1 using Agilent 6890 GC-ECD equipped with Phenomenex ZB-1 column (30 m × 0.25 mm × 1 μm). Analysis of THMs and NDMA has been described in detail elsewhere (Gan et al., 2013; Selbes et al., 2013).