Impacts of Bromide and Nitrogen Wastewater Discharges on Downstream Drinking Water Treatment Plant Disinfection Byproducts

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Abstract

Bromide and nitrogen are wastewater effluent constituents that have raised concern for their potential to affect disinfection byproduct (DBP) formation at drinking water treatment plants (DWTPs) downstream of wastewater discharges. Despite the toxicity of brominated and nitrogenous DBPs, wastewater treatment does not usually remove bromide and nitrogen prior to discharge.

Bromide is a conservative chemical and thus is not removed from surface waters via natural transformations after being released, although it may be diluted. Nitrogen is biologically reactive; it can be transformed and removed by bacteria in the environment and in wastewater treatment plants (WWTPs). While this nitrogen cycling may reduce impacts on downstream DWTPs, it also produces nitrous oxide (N_2O), a greenhouse gas, as a byproduct. Thus, interaction with the environment alters the potential impact of bromide and nitrogen on drinking water systems.

The objective of this work was to examine the impacts of nitrogen and bromide present in wastewater effluent on DBP formation at downstream DWTPs, within the context of current and possible future DBP regulations. Three major conclusions were reached. First, within Southwestern Pennsylvania, an area where surface water bromide concentrations have increased due to fossil fuel extraction-based wastewater discharge, no statistically significant improvement in species-specific risk was observed over the past 20 years, despite decreasing TTHM levels. Second, nitrogen treatment decisions at WWTPs influence the formation of N-

nitrosodimethylamine (NDMA), an unregulated but toxic DBP, at downstream DWTPs in areas of high de facto reuse (DFR). More plants using nitrifying wastewater treatment resulted in significantly lower NDMA detection rates and concentrations observed at chloraminating DWTPs located downstream. Third, the current approach to estimating national emissions of N_2O related to wastewater treatment may underestimate emissions by an order of magnitude. Further, nitrogen removal at wastewater treatment plants reduces total N_2O emissions attributable to wastewater treatment by reducing the N_2O that would be generated in receiving surface waters. Thus, in both cases, impacts of WWTPs on downstream DWTP DBPs were observable. While natural cycling may remove nitrogen from surface water, in-plant removal of nitrogen prevents large amounts of N_2O emissions.

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Chapter 1 Introduction

The purpose of wastewater treatment plants is to limit environmental damage and human health concerns associated with discharging wastewater to receiving surface waters. Wastewater treatment plants are most frequently designed to remove solids, carbonaceous biochemical oxygen demand (BOD), and pathogens that may be present in the wastewater. However, certain components are not removed in traditional wastewater treatment processes, and others are only required to be removed in areas where surface waters are particularly sensitive to their release. These components may be removed through natural processes or may persist in receiving waters. Once released into surface waters, these components can affect downstream drinking water treatment systems.

Bromide is a contaminant with minimal biological reactivity that is frequently associated with wastewater from fossil fuel activities (e.g., produced water from shale gas development). It has a high toxicity threshold and is expensive to remove; therefore, it is usually not removed in conventional or industrial wastewater treatment. Once discharged, bromide will remain in the surface water. If drinking water treatment plants (DWTPs) are located downstream of wastewater discharges containing bromide, the bromide will be present in the intake water. When this source water is disinfected, usually with chlorine, bromide is incorporated into the resulting disinfection byproducts (DBPs). Previous work has shown that the presence of bromide in source waters increases DBP formation (McGuire et al., 2002) and leads to the formation of more toxic DBPs (Richardson et al., 2007; Echigo et al., 2004; Plewa et al., 2004). Source waters with elevated bromide levels appear to have elevated risk associated with them after chlorination (Regli et al., 2015; Yang et al., 2014; Hong et al., 2007).

Unlike bromide, nitrogen is biologically reactive. Domestic wastewater treatment harnesses microbial communities to treat wastewater. Bacteria grow using the carbonaceous and nitrogenous materials present in the wastewater as energy sources. The organisms are then removed through settling or filtration. Within a wastewater treatment plant, influent nitrogen is almost entirely in ammonia/ammonium (NH_3/NH_4^+) or organic forms (reduced, with an oxidation state of -3) and can undergo a variety of transformations. Nitrification can lead to oxidation of ammonia; first to nitrite (NO_2^-) and then to nitrate (NO_3^-). Denitrification reduces oxidized nitrogen, converting it from nitrate to nitrogen gas (N_2). Nitrification and denitrification can occur incidentally in treatment processes or systems can be specifically designed to enable growth of nitrogen transforming populations. Microbial growth on carbonaceous materials will also assimilate nitrogen within the formed cells. Treatment plants designed to enable both microbial nitrification and denitrification are referred to as biological nitrogen removal (BNR) plants. Figure 1.1 illustrates the basic nitrogen cycle and the primary nitrogen transformations that may occur within a treatment plant**.** For a more in-depth depiction of the nitrogen cycle, see Schreiber et al. (2012).

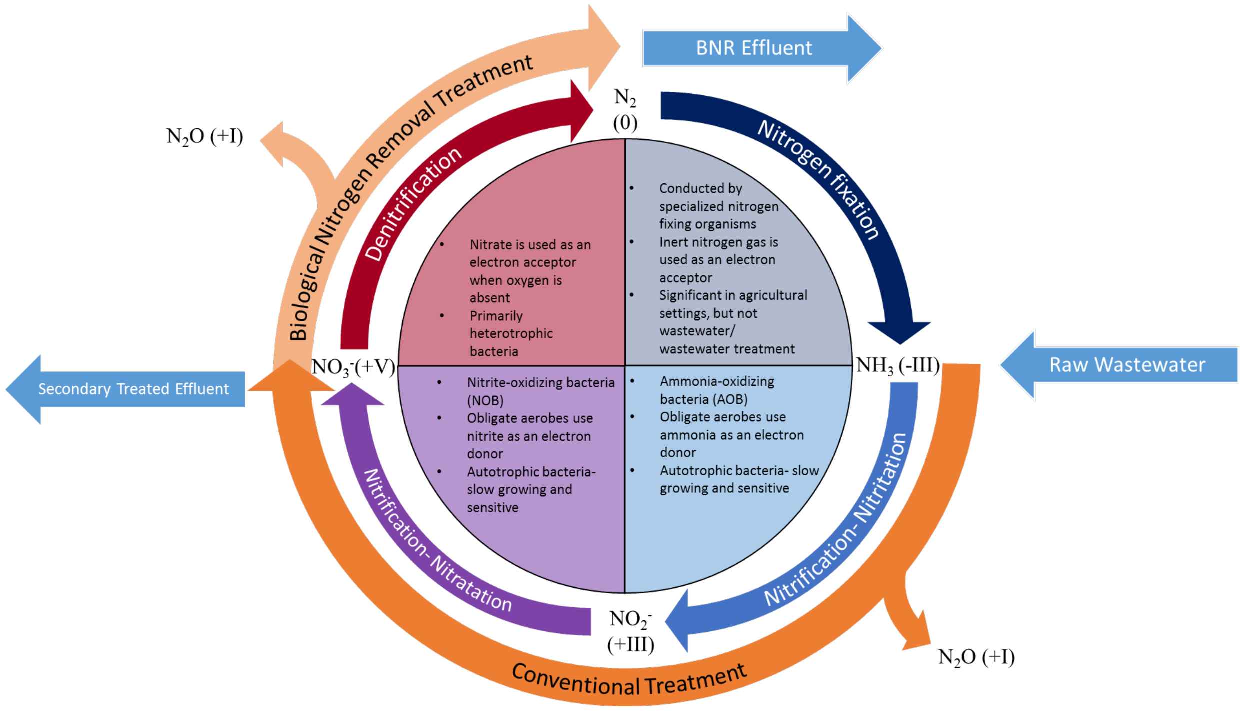


Figure 1.1. A simplified representation of the nitrogen cycle and transformations that my occur at different levels of treatment

Biological nitrogen removal (BNR) is increasingly being used as a means to reduce nutrient discharges into waterbodies (Greening and Janicki, 2006). Nitrogen removal is of particular interest for coastal waters; one prominent example is the Chesapeake Bay Watershed (Hagy et al., 2004; Anderson et al., 2002; Boesch et al., 2001; Bowen and Valiela, 2001). A number of studies have reported the success of BNR implementation in improving surface water quality (Boesch et al., 2001; Kemp et al., 2005). Despite this, in 2012 only about 1.2% of the population of the United States (USEPA, 2014) was estimated to be served by a BNR plant, likely because of the higher cost of treatment associated with biological nitrogen removal (Tchobanoglous and Burton, 1991).

Nitrogen that is not removed in the treatment plant is discharged to the surface water, where the same biological processes (nitrification and denitrification) occur outside of the engineered environment. However, similar to bromide, nitrogenous chemicals that remain in the water long enough to reach a downstream DWTP may influence DBP formation. Nitrogenous DBPs (N-DBPs) are more toxic than their carbonaceous counterparts (Plewa et al., 2008), and N-DBP formation has been linked to nitrogen content of the source water (Kristiana et al., 2017).

While nitrogen may reach downstream DWTPs and influence DBP formation, more so when nitrogen removal is not included in wastewater treatment, some nitrogen will be removed from the water through cycling in both the treatment plant and the receiving water. This removed nitrogen is no longer in the effluent; however, an important byproduct is released into the air: nitrous oxide (N_2O). N_2O is a potent greenhouse gas (GHG) with a global warming potential of about 300 times that of CO_2.

Figure 1.2 illustrates these multiple paths for wastewater discharges to affect downstream DWTPs and the environment.

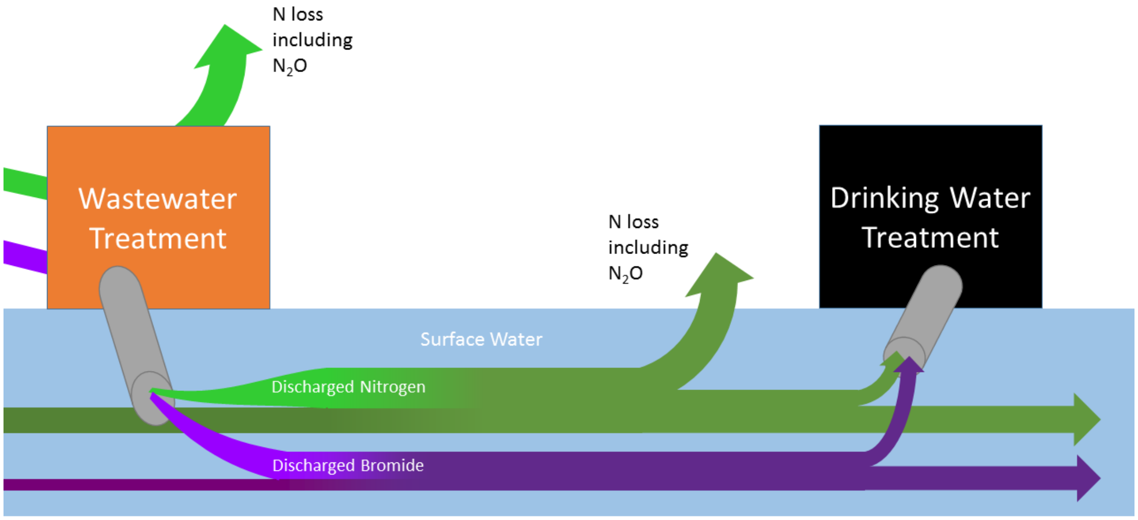


Figure 1.2. Conceptual diagram of wastewater discharge and downstream reuse

Problem Identification

Disinfection byproducts have been shown to be cytotoxic and genotoxic (Yang et al., 2014; Plewa et al., 2008; Muellner et al., 2007; Plewa et al., 2002). Epidemiological work has also linked the consumption of DBPs with cancer (Villanueva et al., 2004; Cantor et al., 1998) and negative reproductive outcomes (Cedergren et al., 2002; Magnus et al., 1999). DBPs at DWTPs are regulated by two surrogate metrics intended to represent a larger pool of unmonitored DBPs: total trihalomethanes (TTHM) and haloacetic acids 5 (HAA5) (USEPA, 2006). Both of these metrics are the sum of the concentrations of a specific class of DBPs, and both sets include species with varying degrees of bromination. However, the elevated toxicity of brominated species relative to their chlorinated analogues raises the concern of whether these metrics are adequate for limiting risk associated with DBPs in areas where bromide discharges have appreciably increased surface water bromide concentrations, such as southwestern Pennsylvania (Good and VanBriesen, 2016; Weaver et al., 2016; States et al., 2013; Wilson and VanBriesen, 2012). Analysis of historical data for this region will enable evaluation of changes in TTHM values, relative bromination, and species-specific risk.

N-DBPs are not federally regulated despite their well-reported toxicity (Plewa et al., 2008; Muellner et al., 2007). WWTP effluent has been previously considered for its potential contribution to downstream DWTP N-DBP formation. The unintentional reuse of discharged wastewater, de facto reuse (DFR), at downstream drinking water treatment plants is becoming more common. Rice et al. (2013) observed increasing volumes of wastewater discharge upstream of the nation's highest DFR DWTPs. N-nitrosodimethylamine (NDMA) is a highly toxic N-DBP that has been detected at DWTPs (USEPA, 2007). Mitch and Sedlak (2004) observed that secondary wastewater effluent contains NDMA precursors in sufficient quantities to form over 100 times the California notification threshold of NDMA (California Division of Drinking Water, 2015). However, Krasner et al. (2009a) observed that nitrification at a WWTP halved the NDMA formation potential (NDMAFP) of the effluent. While NDMA and its precursors have been widely observed in wastewater effluent (Chuang and Mitch, 2017; Lee et al., 2015; Krasner et al., 2009b), analysis of the effect of wastewater discharges and nitrogen treatment on the finished water of downstream DWTPs is lacking. Nitrification may be a valuable tool for reducing NDMA concentrations in drinking water. Examination of historical data for upstream WWTP alongside downstream DWTP NDMA concentrations will provide insight into the impact of wastewater treatment decisions on drinking water NDMA formation.

While nitrogen removal at WWTPs may be important for reducing NDMA formation in drinking water systems, extensive incorporation of such treatment throughout the U.S. may significantly change N_2O emissions that affect climate. The current method of estimating national N_2O emissions from wastewater treatment uses simple, point emission factors to estimate N_2O emissions based on nitrogen mass flows (USEPA, 2014). However, researchers have noted that N_2O emissions from the wastewater treatment environment are highly variable (Rodriguez-Caballero et al., 2014; Foley et al., 2011; Ahn et al., 2010). This raises concerns over the representativeness of these national N_2O estimates. An approach designed to incorporate uncertainty will provide an assessment of the current estimation approach.

Research Objectives

The objective of this research is to examine the impacts of bromide and nitrogen in wastewater discharges on downstream DWTPs. In the case of nitrogen, a biologically reactive contaminant, the impact of transformations and removal upstream of the DWTP are considered. This was accomplished through tasks that explored:

1. Changes in the concentration and speciation of THMs at major DWTPs over the last 20 years in southwestern Pennsylvania, an area with high bromide surface waters;

2. The impact of high DFR and WWTP nitrogen treatment processes on NDMA concentrations in the distribution systems of downstream DWTPs; and

3. Improving the quantification of emissions of N_2O from domestic wastewater treatment and discharge and assessing how they related to nitrogen treatment decisions.

Structure of Dissertation

This dissertation is organized by chapter. Chapter 1 is this introduction. Chapters 2, 3, and 4 cover tasks 1, 2, and 3, respectively. Chapter 5 reviews the conclusions and implications of the previous chapters. Chapter 6 discusses the potential for future work in this area.

Chapter 2 Temporal and Spatial Variability in Bromination of Pennsylvania Drinking Water Disinfection Byproducts

Abstract

Bromide concentrations have been changing in rivers in Pennsylvania due to changes in disposal practices associated with wastewaters from fossil fuel extraction and utilization. Elevated bromide in source waters at drinking water treatment plant intake locations is expected to increase the formation and bromine incorporation of disinfection by-products (DBPs) that present health risks to consumers. Finished water samples from major drinking water distribution systems in Pennsylvania taken during a national sampling effort (1997-1998) were compared with more recent samples from those same systems (2012-2016). Finished water trihalomethane (THM) formation and bromination show little to no change in southeastern Pennsylvania. In southwestern Pennsylvania, bromination increased and species-specific risk estimates show no change despite declining total trihalomethanes (TTHM). Observed decreases in TTHM levels are insufficient to assess effects of changing source water bromide on drinking water safety.

Introduction

Anthropogenic bromide discharges associated with fossil fuel extraction and utilization have been increasing in Pennsylvania (Good and VanBriesen, 2016; Weaver et al., 2016; States et al., 2013; Wilson and VanBriesen, 2012). These discharges are unregulated as bromide has a high human and ecotoxicity threshold (Flury and Papritz, 1993) and therefore poses little risk when discharged to the aquatic environment. However, increased bromide in source waters is well-known to lead to increased formation of carcinogenic disinfection by-products (DBPs) in drinking water (Singer, 2004; Luong et al., 1980). Bromination is linked to elevated toxicity of the formed DBPs (Richardson et al., 2007; Echigo et al., 2004; Plewa et al., 2004; Luong et al., 1980), and the strongest epidemiological data (Chisholm et al., 2008; Villanueva et al., 2007a) are associated with extensive bromination of trihalomethanes (THM) observed in regions with elevated source water bromide. Thus, the presence of bromide in source waters appears to increase the risk associated with use of chlorinated water (Regli et al., 2015; Yang et al., 2014; Hong et al., 2007).

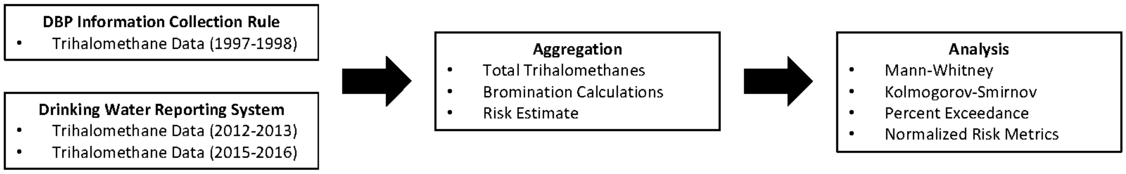
DBP concentrations are widely reported to vary in response to a number of factors, including treatment plant operational conditions and source water differences (Ged and Boyer, 2014). Source and finished water quality in the United States were characterized during the U.S. Environmental Protection Agency (EPA) Information Collection Rule (ICR) (USEPA, 2000a). Higher DBP formation and increased bromination of the DBPs was associated with higher source water bromide; however, significant variability was reported in this study (McGuire et al., 2002) as well as in other occurrence studies (Amy et al., 1994, 1993). Spatial differences in source waters are widely reported, and largely attributed to natural conditions (Zhang et al., 2011). Temporal differences in source waters have recently become of concern, associated with changing climatic conditions or changes in anthropogenic discharges (Wang et al., 2017; Greune, 2014; States et al., 2013; Krasner et al., 1994).

The present study is based on analysis of finished water data for major drinking water treatment systems in Pennsylvania. ICR-based data from 1997-1998 and more recent compliance-reported data for 2012-2016 were used to assess changes in finished water THM concentrations over this time period. Three approaches to estimate risk associated with these changes were used and normalized for comparisons.

Materials and Methods

In the present work, measured THMs in drinking water distribution systems in Pennsylvania from 1997-1998 and 2012-2016 were compared (Figure 2.1). Differences in total trihalomethanes (TTHM), extent of bromination, individual species, and relative risk metrics were considered to assess changes over the nearly two decades.

Figure 2.1. Flowchart for collection and analysis of THM data



Data Sources and Retrieval

Data from the ICR were used as a baseline to compare temporal shifts in THM formation in Pennsylvania. The ICR was a national effort to collect and analyze data on disinfection by-products in drinking water systems; its sampling period ran from July 1997 to the end of December 1998 (18 months) and included drinking water distribution systems that served more than 100,000 people. Samples were analyzed and collected through EPA-approved laboratories (Wysock et al., 2002). The data collected for the ICR has been used extensively in previous literature (Regli et al., 2015; Li et al., 2014; Francis et al., 2010b; Obolensky et al., 2007). THM measurements were collected quarterly. In Pennsylvania, 14 drinking water systems (all using surface water) participated in the ICR (McGuire et al., 2002). *Microsoft Access* was used to access the ICR database (USEPA, 2000a) and extract relevant data. Species-specific THM data (for chloroform, bromodichloromethane, dibromochloromethane, and bromoform) used were for the maximum residence points measured.

More recent data were accessed through the Pennsylvania Department of Environmental Protection (PADEP) Drinking Water Reporting System (DWRS) (PADEP, 2016). The THM species-specific data are the same as are used for compliance monitoring, which requires that samples be collected quarterly from locations in the drinking water system where THM formation is expected to be the greatest. Samples are collected by drinking water personnel and analyzed at PADEP-approved laboratories (PADEP, 2017a).

Sampling Periods

Recent species-specific THM data are available for only 2012 to 2016; prior to this utilities reported only the sum of the species as Total THM. For the comparative analysis, the available recent data were divided into two sampling periods. These sampling periods were selected to replicate the duration and seasonal composition of the ICR data collection effort. Thus, each sampling period started in July (Q3) and ran through the entirety of the following year, for a duration of 18 months. The first sampling period (SP 1) selected aligns with the beginning of species-specific THM data availability on the PADEP DWRS: Q3 2012 – Q4 2013. The second sampling period (SP 2) aligns with the most recent data available at the time of this analysis: Q3 2015 – Q4 2016. Sample sizes by distributions system and sampling period are shown in Table 2.1.

Table 2.1. Sample set sizes by sampling period and PWSID (after quality control)

PWSID	Region	Samples		
		ICR	SP 1	SP 2
3390024	Southeast	5	48	44
3480046	Southeast	2	56	48
7360058	Southeast	9	48	42
7670100	Southeast	5	44	28
5020038	Southwest	3	70	72
5020039	Southwest	12	72	72
5020043	Southwest	5	48	48
5020056	Southwest	5	48	48
5650032	Southwest	5	48	48

Flow Conditions

The ICR data set is the most comprehensive national analysis of source and finished water available; however, concern has been noted about its representativeness due to the unusually warm and wet climactic conditions during 1998 nationally (Roberson, 2002). Further, flow conditions are critical to understand bromide concentration changes as similar loads can lead to different concentrations when flow conditions vary. Major river flow for sampling years were compared with the period of record to inform whether sampling years were outliers. Daily average flow data for sampling periods were retrieved from the USGS National Water Information System (NWIS) for rivers of interest (USGS, 2017). The gages used were USGS 01576000 at Marietta, PA (Susquehanna), USGS 03075070 at Elizabeth, PA (Monongahela), USGS 03049500 at Natrona, PA (Allegheny), and USGS 03086000 at Sewickley, PA (Ohio).

Data Selection

Some systems that were included in the ICR were removed from the analysis after the initial data identification. Two systems were removed because they no longer used chlorine for disinfection and thus comparisons between ICR and more recent TTHM data would be confounded by this significant operational change. One system was removed because recent data were not available from the PADEP DWRS. Two additional systems were removed because they could not be grouped regionally and thus would not contribute to the regional trend analysis. The majority of distribution systems included in the ICR were grouped as either using source waters in the southwestern or southeastern portions of the state, corresponding with large population centers in the Philadelphia and Pittsburgh regions. These regions also have different hydrologic and climactic conditions. The eastern part of the state is part of the mid-Atlantic coastal plain (HUC region 2); the state contains large parts of the Susquehanna (0205) and Delaware (0204) River Basins. Western Pennsylvania is the headwaters of the Ohio River watershed (HUC region 5), which is formed by the Allegheny River (0501) and the Monongahela River (0502). The final analysis included 9 systems; five in the southwest and four in the southeast.

Censored Data and Quality Control

Concentrations below detection are reported as below detection limit or non-detect. This results in a left censored data set common for water quality data. Samples that returned a non-detect for any DBP species were treated as zero (USEPA, 2012b). For the ICR data, non-detects were reported as "-999." These values were replaced with zeros for the statistical analysis. In the more recent PADEP THM data, non-detects are reported in the database as zero.

For sampling events that did not have an entry for all four THM species (incomplete), the data were removed from the analysis for metrics relying on measures from all species, but were included in the individual species analysis (BDCM and DBCM). For instances in which there were duplicate entries, all but one of the entries were removed. There were a total of 11 incomplete sample entries and one instance where a single entry was duplicated 16 times.

Statistical Analysis.

The data retrieved and the calculated metrics were compared across regions and sampling periods. Since the data were left censored and not normally distributed, the median value was taken as the central tendency point of comparison for statistically significant difference. The

Mann-Whitney test with an alpha of 0.05 and a null hypothesis of no difference in the medians was used (Mann and Whitney, 1947). The Kolmogorov-Smirnov (KS) 2 sample test was also used to test for statistically significant differences in empirical distributions (Smirnov, 1948). An alpha of 0.05 was used. This test served as an indicator for similarity of the full spread of the data, rather than just the central tendency.

THM formation and bromination

THM formation and bromination were examined through TTHM, BDCM, and DBCM concentrations as well as bromine substitution factor (BSF) and percent bromination. TTHM is the current metric monitored for compliance (80 ppb is the limit) (USEPA, 2006). BSF, a normalized molar bromine incorporation factor, was developed by Obolensky and Singer (2005). BSF and related incorporation metrics have been widely used to characterize the extent of DBP bromination (Wang et al., 2017; Tian et al., 2013; Hua and Reckhow, 2012; Francis et al., 2010a; Hua et al., 2006; Rathbun, 1996). An alternative to the molar-based bromination is to consider the incorporation on a mass-basis (consistent with the mass-based regulatory standard) (Mao et al., 2014; States et al., 2013; Zhang et al., 2011; Sohn et al., 2006). Percent bromination represents the mass fraction of THM species that contain at least one bromine atom.

Risk characterization

Epidemiological studies report a relationship between chlorinated drinking water and bladder cancer occurrence (Salas et al., 2013; Cantor et al., 2010; Villanueva et al., 2007a; USEPA, 2005b; Villanueva et al., 2004), and regulatory limits have been based on these studies. Laboratory studies have associated bromination of DBPs with increased toxicity (Yang et al., 2014; Plewa et al., 2002). In writing the Disinfectants and Disinfectant Byproducts (D/DBP) rule, the United States Environmental Protection Agency (USEPA) used available data to set a standard for TTHM (USEPA, 2006) as one of two indicator groups (THM and HAA) intended to protect consumers from the wide variety of DBPs formed in chlorination of drinking water. Recently, the World Health Organization (WHO) reported the THM data are equivocal with respect to carcinogenicity, based on recent studies with negative results (World Health Organization, 2017). Thus, WHO recently published recommendations suggesting THM4 species are noncarcinogenic and that much higher levels of THM are acceptable.

In the present work, three methods are used to estimate changes in DBP-associated risk in Pennsylvania. The first approach utilizes species-specific cancer slope factors (CSF) taken from the USEPA Integrated Risk Information System (IRIS) (USEPA, 2016c). More recently developed CSFs have been described by the EPA (USEPA, 2005a); these values are derived from the same primary research studies (NTP, 1989, 1987, 1985) with a change to assumptions regarding exposure. While the present work uses the IRIS values, minimal difference in the relative risk changes described below would be expected through the use of the modified values. The species-specific CSF method assumes response-additive carcinogenic behavior, following the approach the EPA uses for the risk characterization of other chemical mixtures (Hrudey and Charrois, 2012; Wang et al., 2007; USEPA, 2000a, b). Wang et al. (2017) and Kolb et al. (2017) applied this method to THMs. This species-specific approach to estimating risk captures the widely reported differences between chlorinated and brominated DBPs (Yang et al., 2014; Richardson et al., 2007; Echigo et al., 2004). However, it is limited by its consideration only of

THM species and not other DBPs that may be drivers of carcinogenic and non-carcinogenic risk in chlorinated drinking waters.

The second approach to characterize risk for the spatial and temporal comparisons is based on species-specific guideline values derived by WHO (World Health Organization, 2017). These guideline values are considered to be protective of any added toxicity risk over a lifetime of consumption and consider THM4 to be primarily noncarcinogenic. The WHO recommended approach consists of summing the fractions computed by dividing the observed concentration of each THM4 species by its guideline value. The four summed fractions should remain less than or equivalent to 1 for human health protection (World Health Organization, 2017). The guideline values are 300, 60, 100, and 100 ppb for chloroform, BDCM, DBCM, and bromoform, respectively. This approach is limited by its consideration of only THM species and by its focus on non-cancer outcomes, neglecting possible relationships between other DBPs and cancer outcomes.

Finally, a third approach used in this work is based on the odds ratio (OR) method in the Economic Analysis for the Stage 2 D/DBP rule (USEPA, 2005b) as modified recently by Regli et al. (2015). This method is intended to estimate increases in bladder cancer risk from chlorinated drinking water, using TTHM concentration as a surrogate. It does not incorporate species-specific considerations as epidemiological studies on which it is based measured only THM4 and not the individual species. The relationship used is shown in equation 1 (Regli et al., 2015) and plotted in Figure A.1.

$$Added\ Risk = \frac{0.0209*e^{[TTHM]*0.00427}}{1+\left(0.0209*e^{[TTHM]*.00427}\right)} - 0.02047 \qquad \text{(Equation 1)}$$

The Regli OR approach, while unable to account for effects of changing bromination directly, does incorporate some attention to this issue since the brominated DBP contribute more to TTHM due to their higher mass than chloroform.

These three methods represent different interpretations of THM4 species association with a negative health outcome. Specifically, the OR and CSF approaches assume cancer as a health endpoint, while the WHO approach assumes non-cancer endpoints. The focus of this work is not on the quantification of risk based on any of these methods, but rather on the relative changes in these computed risk values spatially and temporally in Pennsylvania. The fact that each approach assigns different weights to each of the THM4 species, and thus leads to a different interpretation of the relative impacts of the THM4 species, allows a broader consideration of the potential for temporal or spatial risk changes than relying on a single risk term, with associated limitations due to assumed targets (cancer or non-cancer) and limited data. The relative weights for different species in the approaches are the cause for differences in perceived trends across space and time. The mass-based *relative* weights (normalized to BDCM toxicity) considered here are shown in Table 2.2.

Table 2.2. Method THM4 species relative weights

Method	**Chloroform**	**BDCM**	**DBCM**	**Bromoform**
CSF	0.00	1.00	1.35	0.13
WHO	0.20	1.00	0.60	0.60
OR	1	1	1	1

The CSF method places all the weight on the brominated species of THM4 (DBCM>BDCM>bromoform; chloroform zero). The WHO method also weighs the brominated forms more heavily, but chloroform receives a nonzero value (BDCM>DBCM=bromoform>chloroform). The OR approach is based on TTHM and thus, gives each THM4 species an equivalent mass-based weight; this weighs the brominated species higher than chlorinated on a molar basis due to the higher mass of bromine relative to chlorine. These risk approaches cannot be directly compared since they have different end-points and target risk levels. In the present work each metric was normalized (by dividing it by its median value in the southeast during the ICR). This allows *relative* comparisons across space and time for each of the metrics.

Results and Discussion

Regional and temporal variations in TTHM were observed in Pennsylvania drinking water systems.

Trihalomethane formation

To provide a national context, TTHM data collected during the ICR in 1997-1998 from southwestern (SW) and southeastern (SE) Pennsylvania were compared to the national ICR TTHM data. The national median was not significantly different from the median in the southeast ($p=0.706$), while southwestern PA represented an area with elevated TTHM during the ICR data collection. The median TTHM for southwest PA (66.5 ppb) was significantly higher ($p=0.000$) than the national (36.5 ppb) and nearly double the southeast PA median (34.2 ppb) during the 1997-1998 sampling.

Figure 2.2 presents results for TTHM for the ICR and the two recent time periods for the southwest (left) and southeast (right). The southwest had a statistically higher TTHM median and different distribution than the southeast for all sampling periods. In the southwest, the median TTHM decreased significantly (p=0.012) from 1997-1998 to 2012-2013 (SP 1=47.9 ppb), and then remained steady in 2015-2016 (SP 2=47.4 ppb). TTHM was unchanged between the ICR and more recent samples in the southeast (SP 1= 32.8 ppb, p=0.222; SP 2= 35 ppb, p=0.536).

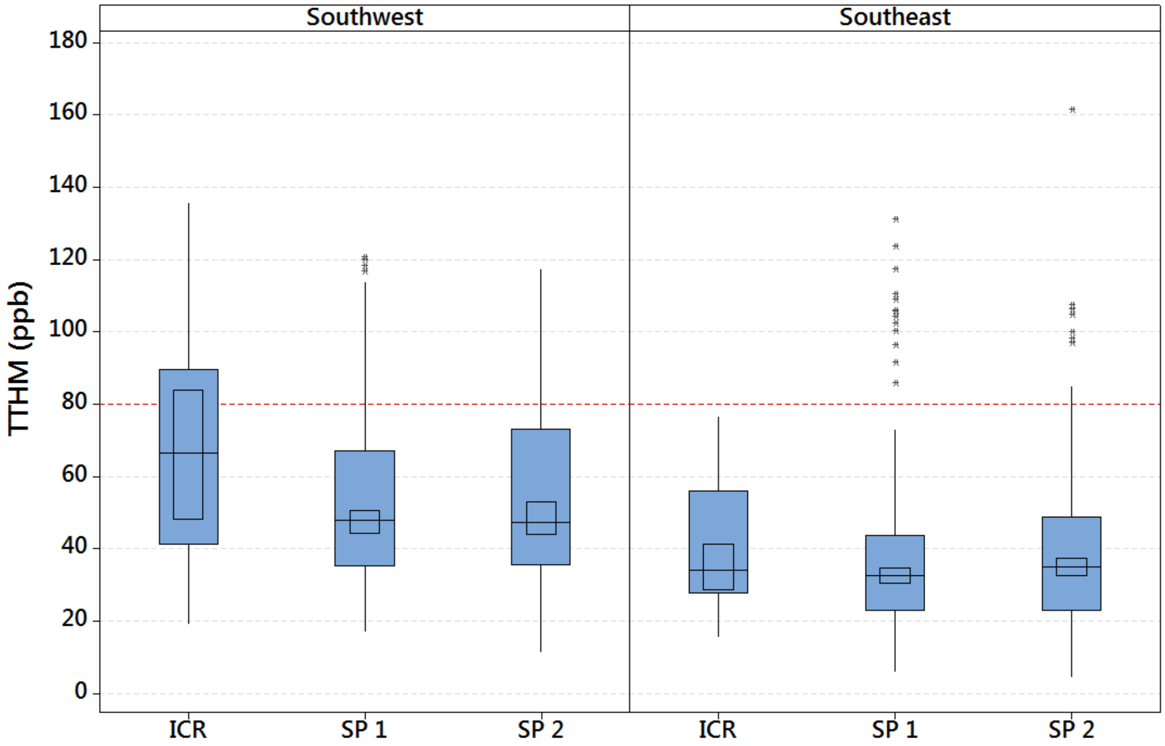


Figure 2.2. TTHM concentrations in large Pennsylvania drinking water systems. ICR represents data from 1997-1998, SP 1 represents data from 2012-2013, SP 2 represents data from 2015-2016

Examination of the full distribution yielded differences in the number of samples that exceeded the maximum contaminant level (80 ppb). In the 1997-1998 sampling, in the southeast, no samples exceeded 80 ppb, while 40% of the samples in the southwest exceeded this threshold. The decrease in TTHM observed for the southwest also led to a decrease in exceedance frequency to 15% (SP 1) and 18% (SP 2). The southeast showed a small increase in exceedance frequency (from 0% to 7% for both SP 1 and SP 2). These results provide insight into how the distribution of TTHM is changing in these systems; however, they represent point measurements, not locational running annual averages (LRAAs), and thus do not indicate compliance violations.

Extent of bromination in THM

The bromine substitution factor (BSF) was used as the primary metric of comparison for THM bromination. The results for all sampling periods and both regions are shown in Figure 2.3.

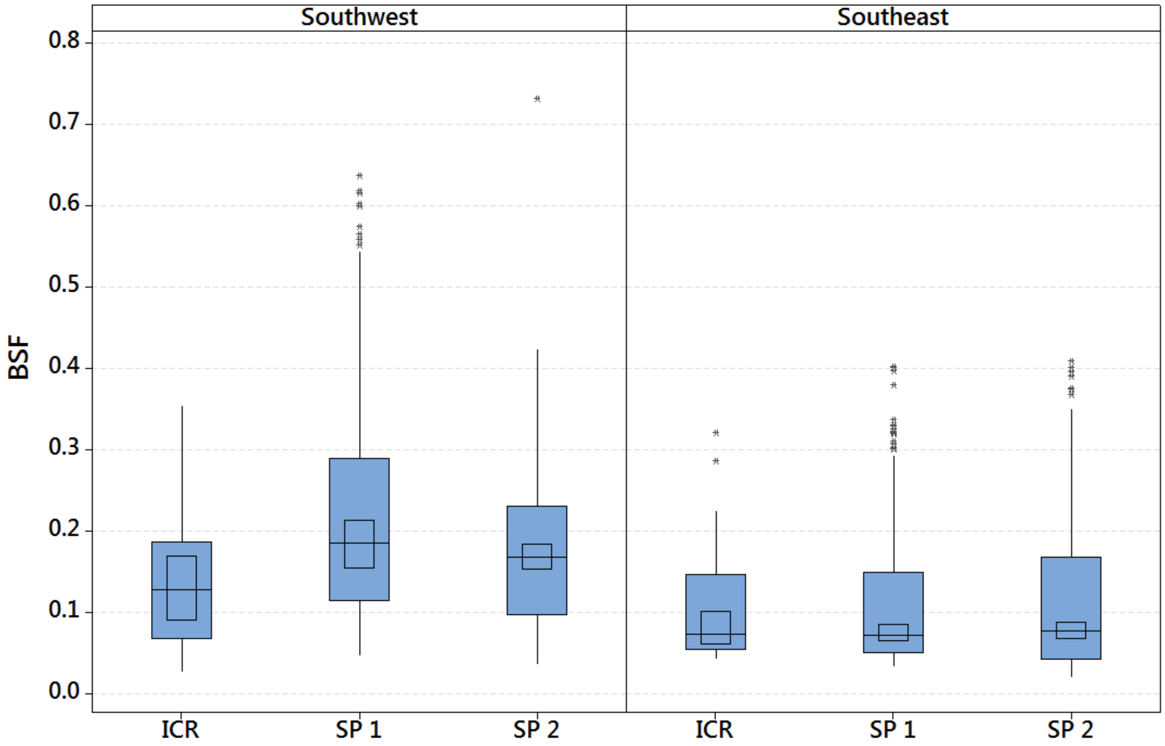


Figure 2.3. Bromide substitution factors computed from THM species-based concentrations in large Pennsylvania drinking water systems. ICR represents data from 1997-1998, SP 1 represents data from 2012-2013, SP 2 represents data from 2015-2016

The data collected in 1997-1998 do not indicate a significant difference in regional medians for BSF (SW 0.13, SE 0.07, p=0.154) or empirical distribution of BSF; this was also true for percent bromination by mass (data not shown). In the southeast, there was no significant difference in median or empirical distribution for either of the two subsequent sampling periods (SP 1 0.07, SP 2 0.08). In the southwest, SP 1 and SP 2 had statistically significantly higher BSF medians, 0.19 (p=0.001) and 0.17 (p=0.039), respectively, than in the southwest during the ICR and in the southeast during any time period. BSF in the southwest peaked during SP 1 and dropped slightly, although not to ICR levels, by SP 2. SP 1 had a statistically significantly different distribution when compared to the ICR and the SP 2 in the southwest. High BSF outliers seen in the southwest were associated with Allegheny River source water while those seen in the southeast were in the Delaware River watershed (Little Lehigh Creek).

Percent bromination by mass followed similar trends to BSF for the median values (data not shown); in the southwest all sampling periods were significantly different, while in the southeast no sampling periods were significantly different. For SP 1, the southwest (51.9%) was significantly higher (p=0.000) than the southeast (25.0%). For SP 2, the southwest (48.0%), was also significantly higher (p=0.000) than the southeast (27.1%). In the southwest, all empirical distributions were significantly different from each other while in the southeast no significant differences were seen.

Individual brominated species

Concentrations of two brominated species of THM, BDCM and DBCM, were also examined. The results are shown in Figure 2.4. Also included in this plot are reference lines for concentrations of BDCM and DBCM associated with risk thresholds of 10^{-5} (6 and 4 ppb, respectively), based on the CSF values (USEPA, 2017a, b).

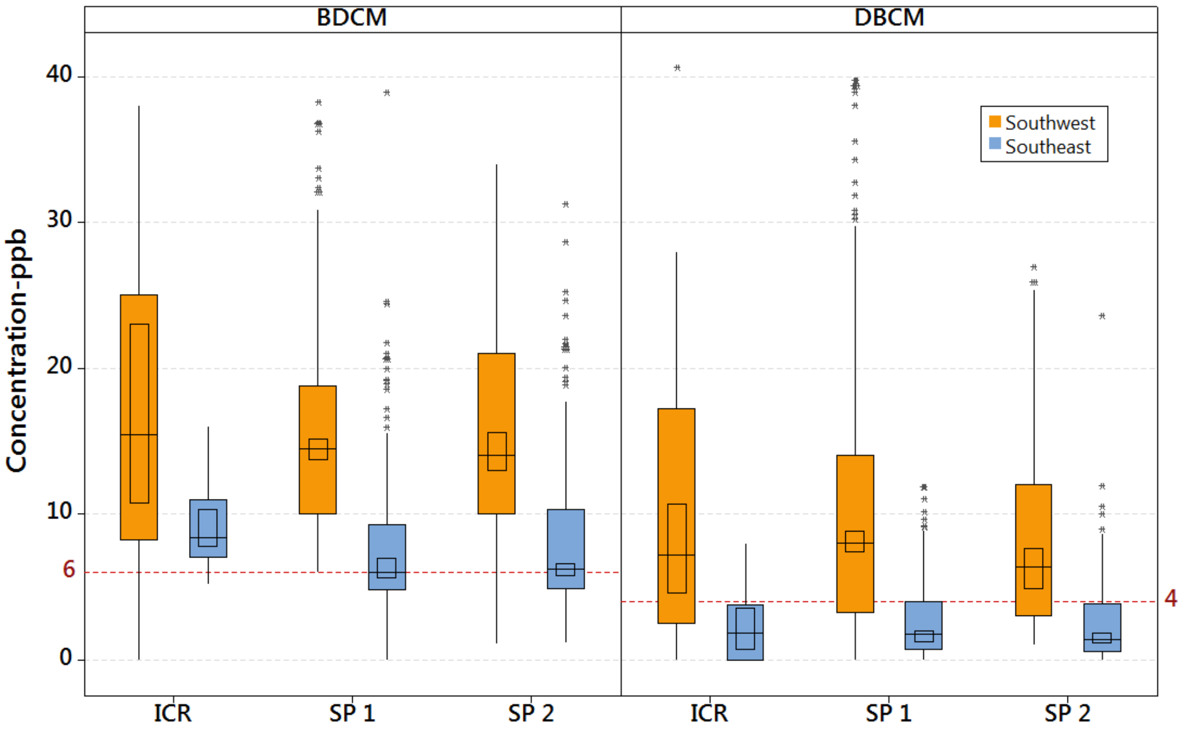


Figure 2.4. BDCM (orange, left side for each sampling period) and DBCM (blue, right side for each sampling period) concentrations in large Pennsylvania drinking water systems. ICR represents data from 1997-1998, SP 1 represents data from 2012-2013, SP 2 represents data from 2015-2016

For all sampling periods, BDCM and DBCM had significantly higher median concentrations in the southwest than the southeast. In the southeast, the median BDCM decreased for both SP 1 (6.0 ppb, p=0.003) and SP 2 (6.2 ppb, 0=0.010) relative to the ICR (8.4 ppb); SP 1 and SP 2 were not different from each other (p=0.512). The distribution for BDCM from the ICR was significantly different from SP 1 and SP 2. DBCM did not change significantly in the southeast in any sampling period (ICR=1.8 ppb, SP 1=1.7 ppb, SP 2=1.4 ppb) according to both central tendency and distribution tests.

In the southwest, there was no significant decrease for either SP 1 or SP 2 relative to the ICR medians for BDCM (15.4 ppb, SP 1 p=0.588, SP 2 p=0.702) or DBCM (7.2 ppb, SP 1 p=0.577, SP 2 p=0.773). For BDCM, SP 1 (14.5 ppb) was not significantly different (p=0.807) from SP 2 (14.0 ppb) by median or distribution test. For DBCM, SP 2 saw a significant decrease (p=0.029) in median relative to SP 1 (8 to 6.4 ppb). The lack of a significant decrease in BDCM and DBCM concentrations in the southwest is particularly notable given the moderate decrease in TTHM over the same time periods (a nearly 20 ppb decrease in the median). Also worth noting is that the observed concentrations for DBCM and BDCM for the southwest show greater variability (wider spread of data shown in Figure 2.4) than in the southeast. These results may indicate more variability in bromide concentrations in southwestern surface waters or may reflect differences in treatment systems in drinking water plants in southwestern Pennsylvania.

Risk

The empirical distributions for response-additive CSF risk are shown in Figure 2.5. For every sampling period, the response-additive risk calculated in the southwest was significantly higher than in the southeast (ICR p=0.003, SP 1 p=0.000, SP 2 p=0.000). In the southeast, the median risk in SP 2 represented a significant decrease from the ICR (p=0.033), which is notable since the TTHM levels did not change significantly. The median value from SP 1 was not significantly different from either of the other periods. None of the empirical distributions were significantly different from each other.

In the southwest, none of the median response-additive risks were significantly different (ICR-SP 1 p=0.814, ICR-SP 2 p=0.769, SP 1-SP 2 p=0.118), and none of the empirical distributions were significantly different from each other. This is particularly noteworthy because it demonstrates a lack of a decrease in response additive cancer risk in the southwest despite a 20 ppb decrease in the median TTHM.

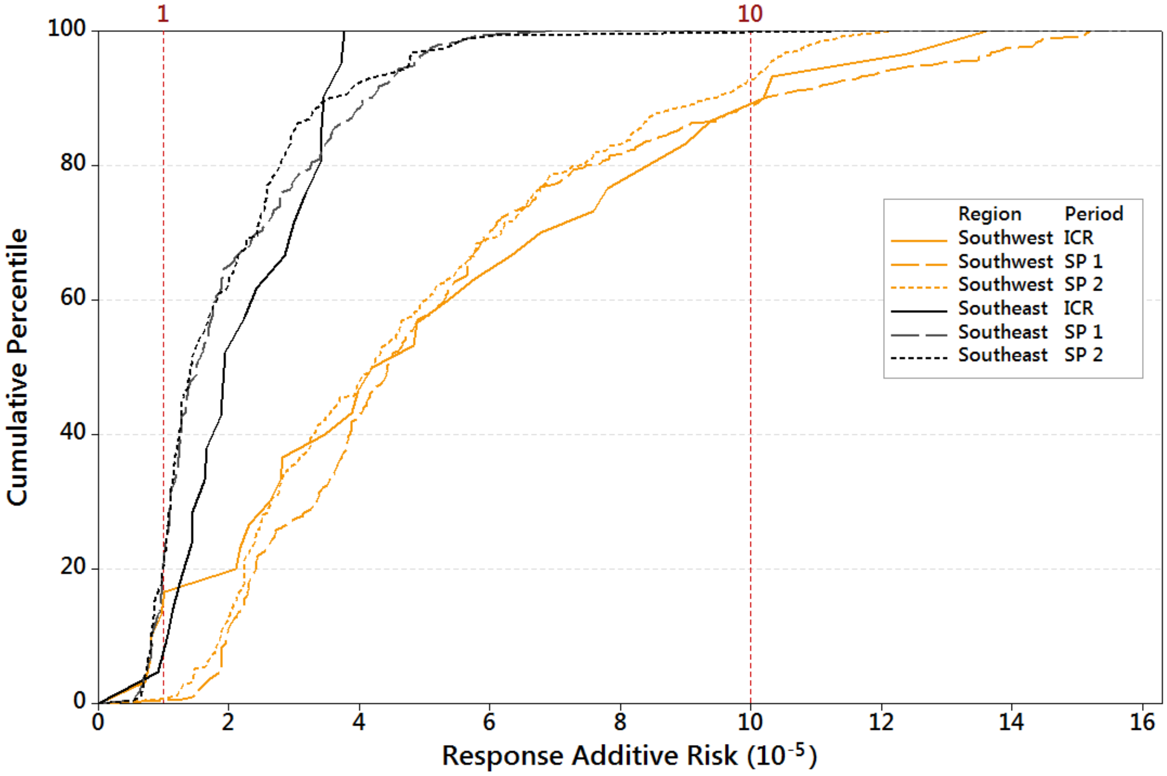


Figure 2.5. Empirical distributions for response-additive risk for different regions and sampling periods. ICR represents data from 1997-1998, SP 1 represents data from 2012-2013, SP 2 represents data from 2015-2016

For the approach described by the World Health Organization, the fraction sums were significantly higher in the southwest than in the southeast for every sampling period. In the southeast, the ICR median was significantly higher than the SP 1 median (p=0.033), but no statistically significant difference in empirical distributions was found. In the southwest, there was no significant difference found between medians of the ICR, SP 1, and SP 2 sampling periods for the WHO-based metric (ICR-SP 1 p=0.371, ICR-SP 2 p=0.174, SP 1-SP 2 p=0.352). None of the empirical distributions were different from each other.

The WHO approach states that the sum of each THM4 species concentration divided by its respective guideline value should remain at or below 1. The only sampling periods that had exceedance of this threshold were in the southwest during the ICR (7%) and SP 1 (5%). Thus, while the trends remained similar to the CSF approach, the values seen in this case generally remained below the threshold of concern.

As the species-specific metrics previously described are not directly comparable due to their different interpretations of THM4 species toxicity, a normalized comparison of the metrics was included. The OR approach was included here for comparison. OR uses only TTHM as an input and thus represents an even weight applied to all THM4 species. The comparison of the metrics normalized to their respective median values in the southeast during the ICR is shown in Figure 2.6.

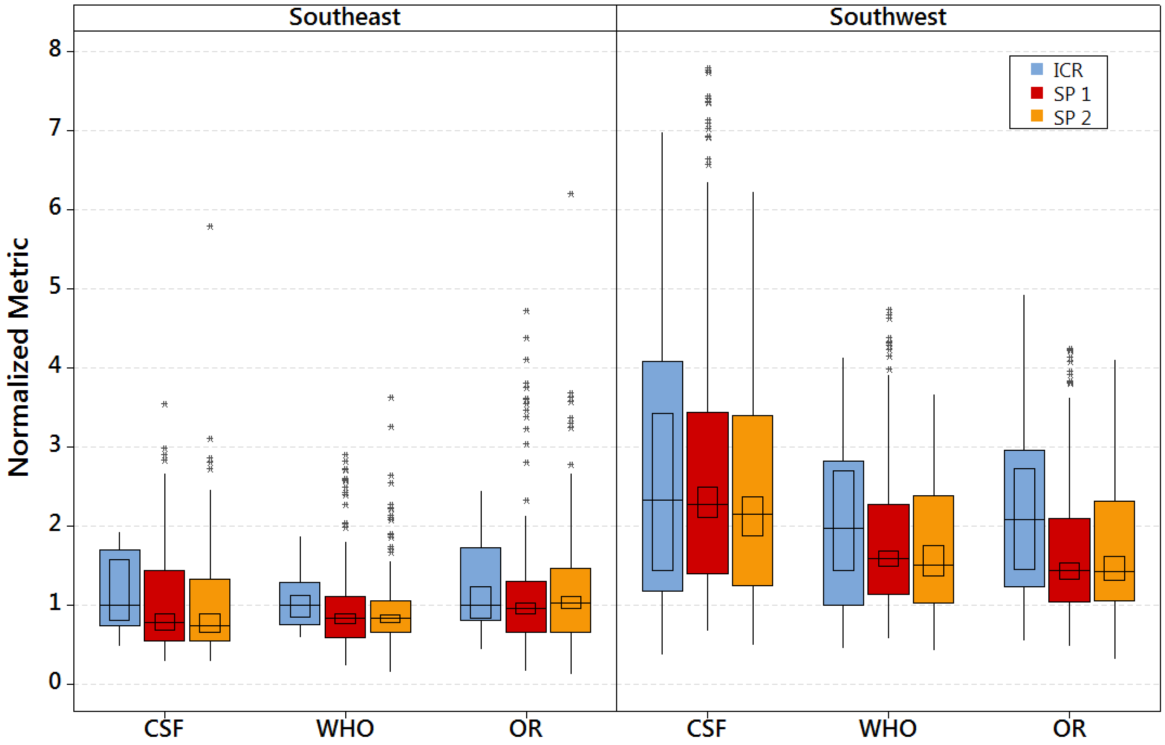


Figure 2.6. Metrics of concern for THMs normalized to median value in southeast during ICR (each method left to right: ICR, SP 1, SP 2)

In the southwest, for OR, SP 1 and SP 2 were significantly lower than the ICR (p=0.012, p=0.016, respectively). This improvement is in contrast with the WHO and CSF approaches, which indicated no significant improvement in the southwest since the ICR. This difference stems from different weights assigned to the THM4 species (see Table 2.2). Specifically, the valuation of chloroform relative to the brominated species. The CSF approach, which places the largest weights on the moderately brominated species (BDCM and DBCM), not only saw no significant improvement in the southwest, but median values in the southwest also remained greater than twice the median ICR value in the southeast. The OR, on the other hand, which weighs each species equally, indicated a large improvement, which was related to the chloroform reduction in the southwest (and corresponding reduction in TTHM). Further, as was shown with the CSF and WHO results, even if metrics demonstrate similar trends, they may call for varying levels of concern. The results are largely dependent on the interpretation of the THM4 species health effects and the use of THM4 as a surrogate for unmonitored and unregulated contaminants that may cause toxicity and carcinogenicity in drinking water.

Flow across sampling periods

Since TTHM formation is driven by a number of source water factors (DOC, temperature, bromide) that can be affected by changes in climate and flow, it is important to assess these conditions for the sampling periods. It has previously been reported that 1998 was a warm and wet year across the United States (Roberson, 2002). However, river flows within Pennsylvania indicate the median flow in the Allegheny, Susquehanna and Ohio rivers were lower during the ICR (1997-1998) than during the more recent sampling (2012-2016). In the Monongahela, river flow during the ICR was significantly lower than during SP 1 (2012-2013) but not significantly different than during SP 2 (2015-2016). Thus, in no case did flow analysis indicate climactic conditions in southwest Pennsylvania during 1997 or 1998 would have diluted bromide. Rather, if loads remained similar, increased flows in the more recent periods would have been expected to dilute bromide, leading to lower bromide concentrations and less bromination of DBPs in the recent periods. Thus, the increased bromination of DBPs in southwestern Pennsylvania cannot be explained due to flow changes. As previously reported, increasing anthropogenic bromide loads are the likely cause of changing THM bromination in these rivers (Wang et al., 2017; Wilson and VanBriesen, 2014; States et al., 2013; Wilson et al., 2013).

The empirical cumulative distributions for yearly (calendar) average flows during the period of record of major rivers in Pennsylvania are shown in Figure 2.7; years associated with the previously described sampling periods are labeled.

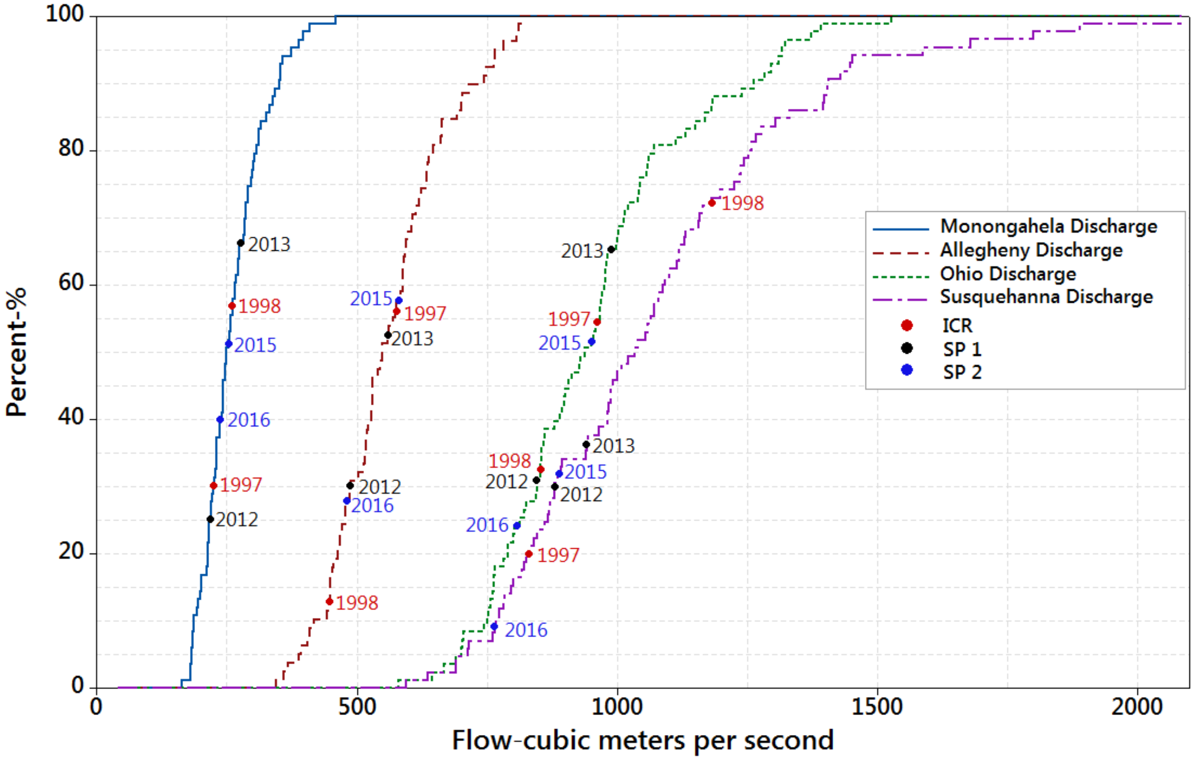


Figure 2.7. Cumulative distribution function of yearly average flow for major rivers in Pennsylvania

The majority of year and river combinations remained within the middle 60% (20th percentile to 80th percentile). The only two exceptions were for lower flow conditions in 1998 on the Allegheny (13th percentile) and 2016 in the Susquehanna (9th percentile). These conditions could have led to higher organic carbon or bromide concentrations in the source waters due to concentration and higher temperatures due to lower depths or slower flows in these systems.

The lower flow in the Allegheny River in 1998 could have led to elevated brominated DBPs for several drinking water systems in the ICR collection period (and thus elevated TTHM). This might have made the change observed in TTHM (decreases) less significant, and it might have masked an even greater increase in bromination between 1998 and the present.

The unusually low flow in the Susquehanna River in Fall 2016 due to drought conditions (Hess, 2016) was observed to lead to increased bromide (National Water Quality Monitoring Council, 2017; PADEP, 2017b) and could have altered DOC. These changes would be expected to increase the concentration and bromination of the formed TTHM. However, as reported above, in SE PA, no significant changes in TTHM or bromination were observed between the 1997-1998 and 2013-2016 periods. It is possible that these unusually low flows masked what could have been a decrease in TTHM or bromination if flows were more typical.

Conclusions

Since the USEPA's ICR for DBPs in 1997-1998, Pennsylvania's large drinking water distribution systems have undergone significant process changes and have experienced changes in source water quality (especially with respect to bromide). In the southeastern part of the state, which had TTHM similar to national median values during the ICR period, TTHM has not changed significantly: TTHM concentration and the bromine substitution factor remain low and similar to values reported during the ICR. The southeast saw a small but statistically significant decrease in BDCM, leading to slightly lower risk computed with cancer slope factors.

In the southwest, a substantial decrease in TTHM in finished water is reported since the ICR (about a 20 ppb drop in the median). Despite this, there has not been a significant decrease in the THM species with intermediate bromination (BDCM and DBCM), often considered the species of highest concern, since the ICR. This is also reflected in a significant increase in the bromine substitution factor and no improvement in water quality according to metrics prioritizing brominated species (CSF and WHO approaches). Thus, the declining TTHM was all associated with decreased chloroform and did not lead to a reduction in species-specific risk in the region that has experienced increasing source water bromide concentrations.

Chapter 3 Impact of Nitrogen Removal in Wastewater Treatment on DBP Formation at Downstream Drinking Water Treatment Plants

Abstract

De facto reuse (DFR) occurs when the receiving water for wastewater effluent is used as source water by a downstream drinking water treatment plant (DWTP). Wastewater effluent contains high concentrations of precursors for N-nitrosodimethylamine (NDMA), a toxic disinfection byproduct. Nitrification at wastewater treatment plants (WWTPs) reduces NDMA precursors in this effluent. The present work examines NDMA concentrations in the distribution systems of 31 DWTPs subject to high percentages of DFR. The WWTPs contributing to this DFR were categorized by extent of nitrogen treatment: no intentional nitrogen treatment, nitrification, or nitrification-denitrification. The fraction of upstream effluent discharges receiving nitrogen treatment was calculated and the relationship between this fraction and observed NDMA concentrations was assessed. Results indicate that high DFR DWTPs with large fractions of wastewater undergoing nitrification upstream had NDMA concentrations comparable to a representative national sample of plants. High DFR plants with little upstream nitrification had elevated NDMA detection rates and concentrations, dependent upon the distance between the upstream WWTPs and the downstream DWTP. This suggests that WWTP nitrification may be a valuable process for reducing NDMA concentrations at chloraminating DWTPs in high DFR areas.

Introduction

De facto reuse (DFR) is the unplanned reuse of discharged wastewater effluent that occurs when the receiving body of water is used as a drinking water source downstream. Rice and Westerhoff (2015) concluded in a nation-scale study of 1,210 drinking water treatment plants (DWTPs), each serving more than 10,000 people, that roughly 50% of the plants were affected to some degree by DFR. Further, Rice et al. (2013) observed that, in 2008, higher volumes of wastewater affected the 25 most DFR-impacted DWTPs identified by United States Environmental Protection Agency (USEPA) nearly thirty years earlier (Swayne et al., 1980). The number of drinking water plants affected by DFR and the volume of wastewater affecting them are likely to increase further in the future with increasing urbanization and population growth in the United States. Thus, chemicals that persist through wastewater treatment (e.g. nutrients or pharmaceuticals) may reach more drinking water intakes.

A primary concern surrounding DFR has been the potential for wastewater effluent to affect disinfection byproduct (DBP) formation at downstream DWTPs (Krasner et al., 2013; Krasner et al., 2009a; Krasner et al., 2008; Mitch et al., 2004), or to directly contribute DBPs from the disinfection of treated wastewater (Schreiber and Mitch, 2006). DBPs are formed when organic matter reacts with a disinfectant being used at a treatment plant. These by-products are toxic (Plewa et al., 2008; Richardson et al., 2007; Plewa et al., 2004; Plewa et al., 2002), and DBPs in treated water have been associated with cancer (Villanueva et al., 2007b; Villanueva et al., 2004) and negative reproductive outcomes (Cedergren et al., 2002; Magnus et al., 1999) in epidemiology studies. Two classes of DBPs are currently regulated: trihalomethanes (THMs) and haloacetic acids (HAAs) (USEPA, 2006), and these are considered surrogates for hundreds of unmeasured and unregulated DBPs, that are potentially the source of observed health risks. Source water characteristics affect the nature and concentration of DPBs formed (Kristiana et al., 2017; Roccaro et al., 2011). The presence of nitrogen can result in the formation of nitrogenated disinfection byproducts (N-DBPs) (Sgroi et al., 2018; Kristiana et al., 2017; Singer, 1994), which are more toxic than carbon-only DBPs (Plewa et al., 2008; Richardson et al., 2007).

Municipal wastewater discharges are a significant source of nitrogen, which raises concerns for N-DBPs in chlorinated effluent as well as the potential for increased N-DBP formation at downstream DWTPs. A key group of N-DBPs associated with wastewater and disinfected wastewater effluent are the highly toxic N-nitrosamines, including N-nitrosodimethylamine (NDMA) (Zeng et al., 2016; Gerrity et al., 2015; Lee et al., 2015; Russell et al., 2012; Schreiber and Mitch, 2006). Domestic wastewater serves as a significant source of organic and inorganic nitrogenous compounds, which include precursors to NDMA formation (Mitch et al., 2004); common secondary-treated wastewater effluent contains sufficient NDMA precursors to form concentrations of over 1,000 ng/L NDMA under ideal NDMA-forming conditions (Hanigan et al., 2012; Mitch and Sedlak, 2004). In addition, NDMA forms during wastewater treatment disinfection and thus is frequently observed in wastewater treatment plant (WWTP) effluent (Chuang and Mitch, 2017; Dai et al., 2015; Lee et al., 2015; Krasner et al., 2009b; Mitch and Sedlak, 2004). In some watersheds wastewater effluent is the dominant source of NDMA and its precursors when compared to other sources: agricultural runoff, stormwater runoff, and algal blooms (Sgroi et al., 2018; Zeng et al., 2016).

NDMA has become a significant DBP of concern in drinking water as well, particularly at treatment plants using chloramine as a disinfectant (Krasner et al., 2013; Russell et al., 2012; Richardson et al., 2007; Mitch et al., 2004). NDMA is not currently regulated; however the California Department of Public Health (now the California Division of Drinking Water) set a notification level of 10 ng/L (ppt) in drinking water (California Division of Drinking Water, 2015). The U.S. EPA has included NDMA on the Contaminant Candidate List (CCL) 3 and 4 (USEPA, 2016b, 2009); these lists include chemicals that occur in public water systems and may require future regulation under the Safe Drinking Water Act (SDWA). NDMA is considered a probable human carcinogen and has an estimated 10^{-5} risk threshold of 7 ng/L from the consumption of drinking water (USEPA, 1987; Peto et al., 1984). Occurrence data indicate NDMA is the most frequently detected nitrosamine in drinking water, with 27% of plants included in the Second Unregulated Contaminant Monitoring Rule (UCMR2) reporting detection above the minimum reporting limit (MRL, 2 ng/L) at least once from 2008-2010 (8% of chlorinating plants, 78% of chloraminating plants included in the UCMR2) (USEPA, 2007).

Since wastewater effluent is known to be a large source of NDMA precursors and is also frequently discharged upstream of drinking water intakes, the role of wastewater treatment processes in NDMA precursor removal has been explored. Nitrification reduces NDMA formation potential (NDMAFP) (Gerrity et al., 2015; Krasner et al., 2009a; Krasner et al., 2009b; Krasner et al., 2008; Mitch and Sedlak, 2004) through reductions in hydrophilic natural organic matter (NOM), dissolved organic nitrogen (DON), and ammonia. In laboratory studies, Krasner et al. (2009a) observed a halving of median NDMAFP after “good nitrification” ($NH_3 < 2$ mg/L as N) relative to no nitrification while denitrification was observed to increase NDMAFP relative to nitrification, but decrease it relative to conventional treatment (Krasner et al., 2009a). In-river decay of NDMA precursors has also been observed (Schreiber and Mitch, 2006), likely due to microbial nitrogen transformations. Decay rates in the Quinnipiac River were on the order of multiple days (0.2 d^{-1} for the spring and 0.3 d^{-1} in the summer), and the spring decay rate corresponded to a 3.5 day half-life (Schreiber and Mitch, 2006). This would equate to about 200 miles of travel in the Mississippi River (Schreiber and Mitch, 2006).

Field observations linking wastewater treatment-based effects on finished water NDMA at downstream drinking water treatment plants have not been reported previously. The work presented here examines NDMA formation at high-DFR DWTPs, with a focus on nitrogen treatment levels at upstream WWTPs. The goal was to determine whether treatment decisions at WWTPs lead to lower NDMA formation in downstream DWTPs and whether this effect was mediated by the distance between the WWTP and DWTP. To achieve this goal, DWTPs impacted by DFR were selected and linked with the contributing upstream WWTPs to identify effluent treatment levels. Then a comparative statistical analysis was performed to evaluate trends for NDMA occurrence in relation to the presence of DFR, level of WWTP treatment, and effluent travel distance.

Methodology

NDMA Occurrence Data

DWTP NDMA data were collected (in addition to other nitrosamines) between 2008 and 2010 as part of the UCMR2 screening survey that included *all* public water systems that served more than 100,000 people (398 systems), 320 public water systems serving 10,001 to 100,000 people, and 480 systems serving fewer than 10,000 people (USEPA, 2007). In the present analysis only large (L, 10,001-50,000), very large (VL, 50,001-100,000), and extra large (XL, >100,000) plants were considered (a total of 718 plants).

The UCMR2 data request specified that samples were to be collected at 3 month intervals for a 12 month period between January 2008 and December 2010. Thus, most drinking water system had at least 4 collection dates per sampling location (with multiple locations in the distribution system). NDMA samples analyzed in the present work were limited to those taken at the maximum residence time in the distribution system for plants listing surface water as the water source and using either chlorine or chloramine as the disinfectant. Samples were collected by water utilities following a standard protocol and analyzed using method EPA 521, with a minimum reporting limit of 2 ng/L NDMA (USEPA, 2007; Munch and Bassett, 2004).

For the present work, data from the UCMR2 (USEPA, 2007) were imported into Excel. Extracted data included every sample taken during the UCMR2; prior to analysis, data were filtered by five criteria: the “size” field (only “L”, “VL”, and “XL” were used), “contaminant” (only “NDMA”), “FacilityWaterType” (only surface water, “SW”), “SamplePointType” (only maximum residence, “MR”), and “DisinfectantType” (only those using chlorine “CL” or chloramine “CA”). The “AnalyticalResultValue” field provided NDMA measurement concentrations. This field was left empty when the measure was below the MRL, which was 2 ng/L. For the present statistical analysis, samples below the reporting limit were replaced with 0 ng/L (USEPA, 2012b). Thus, the lowest nonzero value for individual measurements in the analysis presented here was 2 ng/L. This conservative choice will bias the analysis of NDMA concentrations toward lower values, making it less likely that an effect would be observed between upstream treatment and NDMA concentrations.

High DFR DWTP Dataset

Previous work by Rice et al. (2015) identified 145 DWTPs with high de facto reuse (>1% wastewater flow contribution by volume under mean streamflow conditions) at a surface water intake that served a population of more than 10,000 people and participated in the UCMR2 data collection effort (USEPA, 2007). The DFR percentages from Rice et al. (2015) represent the fraction of streamflow at the drinking water intake that was sourced from upstream wastewater discharges under mean flow conditions. Additional information on the nature of the DFR estimate can be found in work by Rice and colleagues (Rice et al., 2015; Rice and Westerhoff, 2015; Rice et al., 2013).

Of the high DFR plants identified and ground-truthed by Rice et al. (2015) with UCMR2 samples that met requirements (max res time, surface water, disinfectant type), those that were identified as having a single surface water intake were included in the present analysis as a “high DFR” set. Those with multiple intakes were excluded since they could confound the assessment of relative contribution from upstream wastewater discharges. If a plant had a sample matching all criteria, but was missing disinfectant information for certain samples, disinfectant information was deduced through disinfectant listed for other samples from the plant and confirmed through consumer confidence reports, if possible. If the disinfectant remained unclear, the sample was excluded. Note that this was not done with the full UCMR2 data set because of the large number of treatment plants.

Plants with intake locations that could not be confirmed or potentially significant contributions from WWTPs in Mexico or Canada (for which treatment data were not available) were not considered. The resulting high DFR subset was a group of 31 DWTPs; details are provided in Table B.1 and plant locations are identified in Figure B.1.

High NDMA Plants

DWTPs in the high DFR set that produced high NDMA values (averages above the California notification level of 10 ng/L) were examined separately. USGS gauges (USGS, 2017) were used to examine the source water stream flow in the time leading up to the sample collection date (provided in the UCMR2). Since NDMA samples were taken at the point of max residence time in the distribution system, it is assumed that there would be a lag time on the order of days between source water extraction and sample date. The flow data in the time leading up to the sampling event were qualitatively compared with NDMA concentrations to assess whether high NDMA measures corresponded with source water conditions where flow was below the mean annual average; low flows could cause higher concentrations of NDMA precursors to be present in the source water through simple concentration. These plants are shown in bold in Table B.1.

Clean Water Needs Survey (CWNS) data

WWTP flow and treatment data were taken from the 2008 Clean Watersheds Needs Survey (CWNS) (USEPA, 2012a). The CWNS is conducted every four years and is designed to assess the financial needs of the nation’s wastewater treatment and collection systems. The 2008 CWNS was selected because it was the survey taken nearest in time to the NDMA collection in the UCMR2. In this survey, wastewater treatment plant operational data is collected, including design capacity flow, actual flow, and treatment processes (ammonia and nitrogen removal). For the present analysis, actual ("existing") plant flows reported in the CWNS were used to calculate the flow-based fraction of upstream wastewater discharges that had been treated with some degree of advanced nitrogen treatment. Plants that indicated that they conducted ammonia removal but not nitrogen removal are referred to here as nitrifying plants. Plants that included nitrogen removal as well as ammonia removal are described here as denitrifying.

While wastewater effluent discharges are a primary source of NDMA precursors to surface water (Sgroi et al., 2018; Zeng et al., 2016), they are not the only source of nitrogen present in the water. This work does not account for additional discharges, such as from non-point sources. These sources may influence NDMA formation; however adequate data to quantify their role is lacking.

Identifying Upstream Treatment Type for High DFR DWTPs

In order to compare NDMA formation at DWTPs with upstream wastewater treatment, contributing upstream WWTPs had to be identified. This was accomplished through use of the map component of the De facto Reuse Incidence in our Nations Consumable Supply (DRINCS) ArcGIS model, as produced by Rice and colleagues (Rice et al., 2015; Rice and Westerhoff, 2015; Rice et al., 2013). This model spatially links wastewater treatment plant discharge points and drinking water intake locations with USGS hydrologic flowpaths. Identification numbers for both DWTPs (PWSID) and WWTPs (CWNS ID) were presented in the ArcGIS map. Using the map, the USGS flowpaths were used to trace upstream of drinking water intakes (identified by

PWSID) and identify all discharging wastewater treatment plants by their CWNS identification numbers. Flow and treatment data for these WWTPs were available in the CWNS. Boundaries were limited to the United States.

Wastewater treatment plants with CWNS identification numbers that were not found in the 2008 CWNS were not included in the analysis; 337 wastewater plants were excluded from analysis, representing 9.7% of the all unique upstream plants observed. To examine whether the missing plants were likely to amount to significant unaccounted flows, 2004 CWNS flows were used to estimate the flow volumes for the plants missing in the 2008 CWNS. In all but one case, the total flow from excluded WWTPs was less than 5% of the total wastewater flow that was included in this analysis. The only instance for which this was exceeded was at a DWTP in Georgia (PWSID GA1210001). For this plant, upstream WWTPs where 2008 CWNS data were lacking had total estimated flows (from 2004 data) equivalent to nearly 10% of the flows from WWTPs that were included. GA1210001 was a chlorinating plant that did not yield any NDMA detects during the UCMR2, and thus these missing data did not affect the overall results of the analysis.

Wastewater Treatment Metrics

The fractions of wastewater effluent subjected to varying levels of nitrogen treatment was calculated as three metrics: fraction nitrified, fraction denitrified, and fraction nitrogen treatment (Equations 1-3).

$$Fraction\ Nitrified = \frac{WW\ flow\ from\ plants\ with\ ammonia\ removal}{Total\ contributing\ WW\ flow} \qquad \text{(Equation 1)}$$

$$Fraction\ Denitrified = \frac{WW\ flow\ from\ plants\ with\ nitrogen\ removal}{Total\ contributing\ WW\ flow} \qquad \text{(Equation 2)}$$

$$Fraction\ N\ Treatment = \frac{WW\ flow\ from\ plants\ with\ nitrogen\ or\ ammonia\ removal}{Total\ contributing\ WW\ flow} \qquad \text{(Equation 3)}$$

Here the terms “nitrified” and “denitrified” are used exclusively. The fraction nitrified does not include flows that are nitrified prior to being denitrified. Fraction N treatment includes flows from both nitrification-only plants and nitrification-denitrification plants.

Distance Dependence

Effluent organic matter and DBP precursors are known to degrade in surface waters (Chen et al., 2009; Schreiber and Mitch, 2006). Ammonia released in wastewater effluent may volatilize from surface water or be oxidized to nitrate by nitrifying organisms in the receiving water. Oxidized species may be denitrified to N_2 or other gaseous species, such as N_2O. Schreiber and Mitch (2006) noted that NDMA precursors have half-lives of several days in surface waters. Thus, downstream impacts of WWTP effluent discharge may lessen with distance as nitrogen is transformed in the receiving water. To assess the influence of this effect, the present analysis comparing DWTP NDMA concentrations with upstream WWTP nitrogen treatment was replicated with distance-based cutoffs for WWTPs included. For a given distance, both the wastewater flow treated with ammonia or nitrogen removal and the total contributing wastewater flow (as computed in Equations 1-3) were recalculated with only flows from WWTPs within a selected radius from the DWTP intake location. In addition to the initial analysis with no cutoff, radii of 50km, 100km, and 150km were used; these were not intended to mimic flow distances. WWTPs located beyond the radius or that had flow paths outside the radius were removed from the list of contributing plants to the drinking water treatment plant for each radius-based analysis. The counts of contributing WWTPs included in each analysis are shown in Table B.2.

Statistical Analysis and Dataset Representation

Because the left censoring of the data was significant (80% of all extracted UCMR2 NDMA concentrations were below MRL), a quantile-based comparison was selected. The Mann-Whitney test (Mann and Whitney, 1947) for differences in the median was used to test for statistically significant differences between sets of drinking water treatment plants used when comparing high DFR plants and the full UCMR2. An alternative hypothesis that the two medians were unequal was used. For exceedance and detection frequencies, the two sample test of proportions was used with an alternative hypothesis that the two proportions were unequal. For comparisons of distributions, the Kolmogorov-Smirnov 2-sample test for statistically significant differences in empirical distributions was used (Smirnov, 1948). This provided insight on the full spread of the data, and was not limited to the central tendency. In each case an alpha of 0.05 was used for significance.

The Chi-square test was used to compare the categorical drinking water plant size distribution of the high DFR set with the larger UCMR2 set (Pearson, 1900). This was done to examine whether the data sets had differences in plant size composition. An alpha of 0.05 was used.

Correlation analysis was also used to examine the relationships between the extent of treatment metrics and individual sample NDMA measures. In this work, the Pearson correlation was selected (Pearson, 1895). This was used to compare the linear relationships between the extent of treatment and NDMA formation.

To consider the representativeness of the DFR sub-set used for this work, which was selected to have high DFR and also to be limited to single intake plants, we considered whether the subset was similar to the UCMR2 set in terms of size of plants, disinfection type, and location. For size comparison, plants were grouped into L (10,001-50,000), VL (50,001-100,000), or XL (>100,000) (USEPA, 2007).

In the UCMR2 set, the majority (218 of 318; 68.6%) fell in the XL category while 58 (18.2%) and 42 (13.2%) fell in the VL and L categories, respectively. In the high DFR set, the majority (19 of 31 plants; 61.3%) of DWTPs fell in the XL category, while 7 (22.6%) and 5 (16.1%) fell in the VL and L categories, respectively. Thus, the two sets had approximately the same size composition; the general shape of the distribution was the same in the subset and the full UCMR. A Chi-square goodness-of-fit test indicated no significant difference in plant sizes in the high DFR set compared to the UCMR2 plants.

In terms of disinfectant type, across the UCMR2 set, 63% of the DWTPs used chlorine while 39% of plants used chloramine. Some plants used both disinfectants. Among the high DFR plants, 58% of the DWTPs used chlorine while 48% of the plants used chloramine. The higher chloramine usage rate among the high DFR plants was expected as drinking water plants often switch to chloramine to reduce DBP formation, which is expected to be higher in plants receiving elevated inputs of WWTP effluent.

Results and Discussion

The link between high DFR and detection of NDMA in finished water at drinking water plants has been suggested previously (Rice et al., 2015). And, NDMA is well known to be associated with chloramination, for high and low DFR conditions. The UCMR2 data show few NDMA detections in chlorinating plants. For the UCMR2, 25 of 1,082 (2.3%) measurements at a chlorinating plant yielded a detection; within the high DFR subset, 4 of 70 (5.7%) measurements at chlorinating plants exceeded the MRL. For chloraminating plants, NDMA was detected in 330 of 661 samples (~50%) in the UCMR2, while high DFR plants using chloramination reported detections of NDMA in 37 of 56 samples (~66%); this difference was significant (p=0.015). Figure 3.1 shows the empirical cumulative distribution function (CDF) plots for the UCMR2 sample set (solid) and the high DFR plant sample subset (dashed) at chloraminating plants.

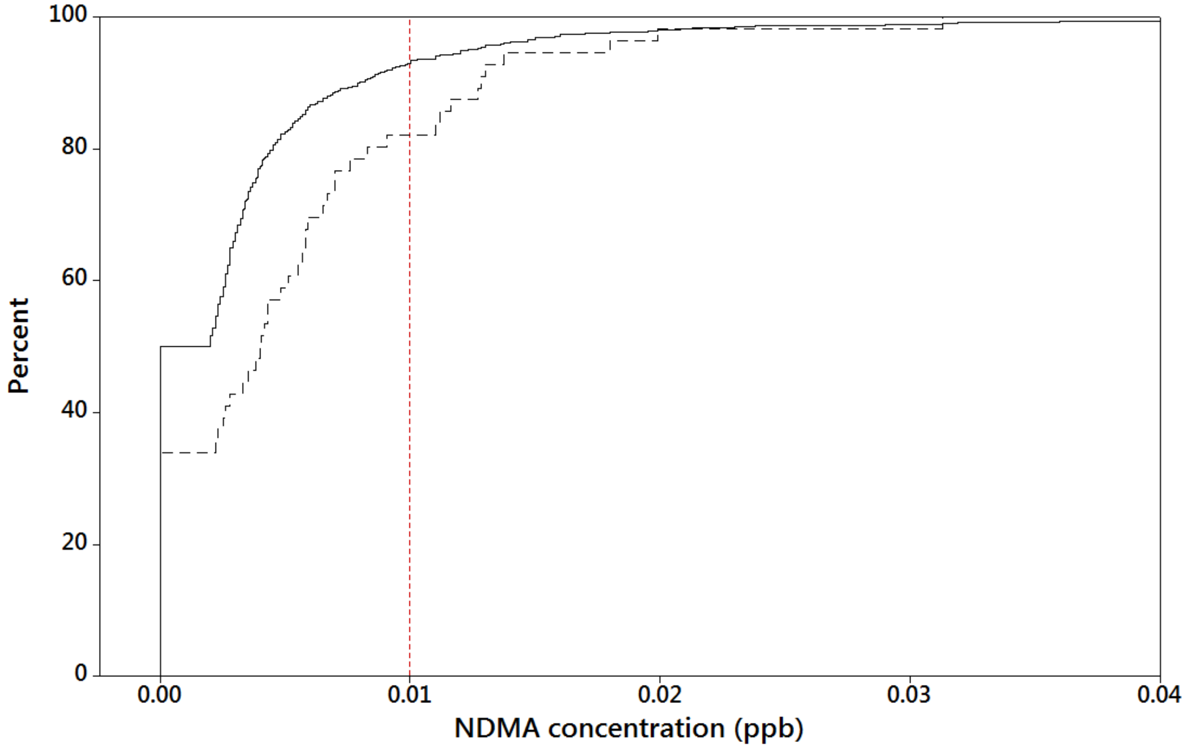


Figure 3.1. Empirical cumulative distribution function (CDF) plots for all chloraminating plants in the UCMR2 set (solid) and in the high DFR subset (dashed). The vertical dashed line represents the California notification level of 10 ng/L

The CDF of the high DFR plants is right shifted relative to the UCMR2, indicating generally higher NDMA measurements at the DFR plants. Further, the two empirical CDFs were statistically significantly different. At the high DFR plants, 18% of the samples exceeded the California notification level of 10 ng/L NDMA (vertical red dashed line in Figure 3.1). In the UCMR2 set, only 7% of samples exceeded this threshold. The exceedance frequency in the high DFR plants was significantly higher (p=0.037). Figure 3.2 is a boxplot of the detected NDMA values for all plants in the UCMR2 and for plants in the high DFR subset; again, only sites using chloramination are shown.

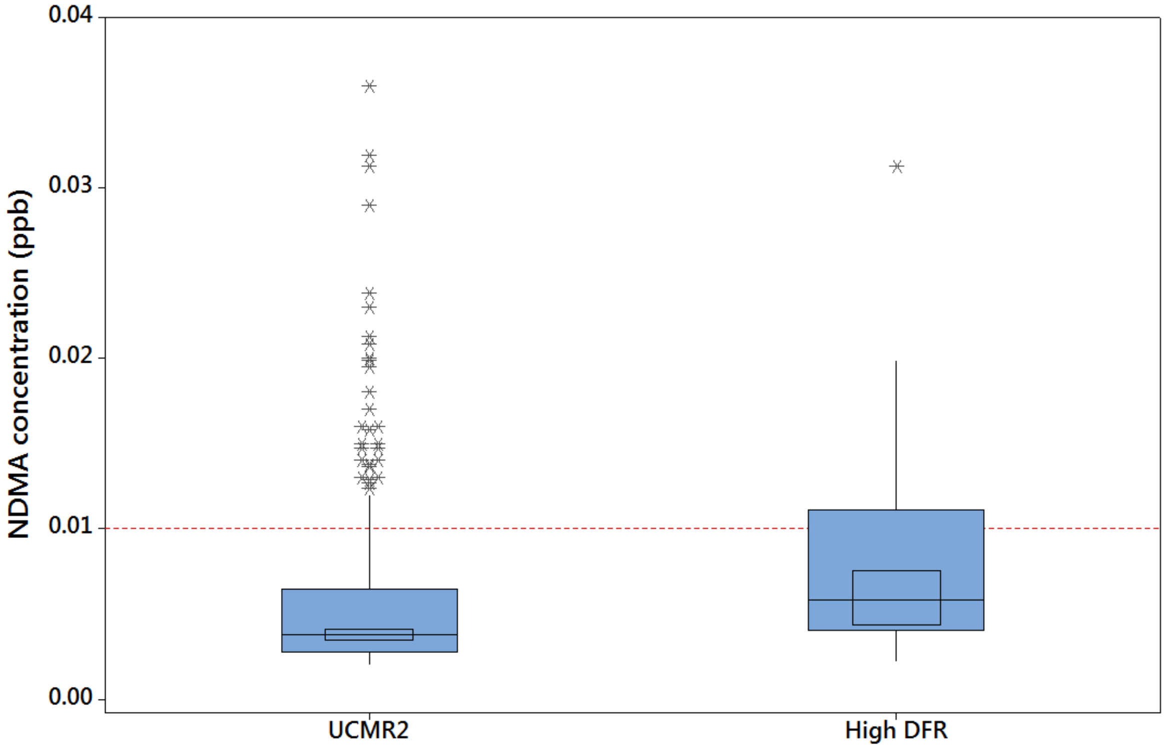


Figure 3.2. Box plot of NDMA detected concentrations at UCMR2 plants and the high DFR subset. The median value is represented by the line within the box, while the extents of the box represent the 75th and 25th percentile and the whiskers extend from up to1.5 times the interquartile range from both the 25th and 75th quantile. Stars represent outliers beyond the interquartile range. The internal box represents the 95% confidence interval for the median. The horizontal red dashed line represents the California notification level of 10 ng/L.

Detectable NDMA measurements at the high DFR plants were statistically significantly higher than in the full UCMR2 set. The median detection at high DFR plants (5.8 ng/L) was significantly higher (p=0.001) than the median detection in the UCMR2 set (3.8 ng/L). Further, the distributions in the two sets were significantly different, with the high DFR distribution being right shifted (higher NDMA) relative to the UCMR2 distribution (see Figure B.2). The high DFR plants had higher NDMA detection frequency, higher NDMA concentrations, and more values that exceeded the California 10 ng/L threshold; thus, DFR is associated higher finished water NDMA formation in chloraminating DWTPs.

High NDMA Values

Three chloraminating plants with average NDMA values above 10 ng/L were considered separately; all had intakes in close proximity on the Mississippi River. Nine of the twelve samples collected by these plants were collected during periods in which flow was lower than the annual mean for the period of record. However, there was no apparent pattern in NDMA concentrations relative to the flow rate of the Mississippi in the time leading up to sampling. Samples taken during lower flow periods, where higher DFR would be likely, did not produce higher NDMA measurements.

Impact of WWTP treatment on DWTP NDMA formation

The present work is designed to evaluate whether choices at the upstream wastewater treatment plants alter the potential for NDMA formation, evaluated by the concentration detected at the maximum residence time in the distribution system.

Three treatment metrics, fraction nitrification, fraction denitrification, and fraction nitrogen treatment, were compared through correlation analysis with measured NDMA concentrations at the maximum residence time location. The results across all analyses for drinking water plants using chloramine are shown in Table 3.1.

Table 3.1 Correlations between NDMA and wastewater treatment metrics for chloraminating DWTPs

	Fraction Nitrified	Fraction Denitrified	Fraction Nitrogen Treatment	
Unconfined	0.119 0.381	-0.018 0.898	0.092 0.501	Pearson Correlation P-Value
50km	-0.186 0.17	-0.005 0.971	-0.169 0.213	
100km	-0.303 0.023	-0.098 0.473	-0.285 0.033	
150km	-0.344 0.009	0.031 0.822	-0.253 0.06	

Light, medium, and dark green represent correlations significant at an alpha of 0.10, 0.05, and 0.01, respectively

No correlations were observed between any extents of treatment and NDMA in the unconfined or 50km analyses. Correlations were seen, however, when using radii of 100km and 150km. At 100km, both the nitrified fraction of wastewater and the fraction of nitrogen treatment were significantly inversely correlated with NDMA concentrations (p values shown in Table 3.1).

In the 150km analysis, NDMA formation was not significantly ($p \leq 0.05$) correlated with percent nitrogen treatment. However, percent nitrified treatment had an inverse correlation with NDMA significant at an alpha of 0.01. As expected, upstream wastewater nitrification has the strongest effect on downstream drinking water NDMA formation. While the distance restriction method included here is insufficient to account for wastewater effluent travel times, these results demonstrated the expected dependence of DFR impact on distance between wastewater effluent discharge and DWTP intakes. The analysis that included all WWTPs may have included wastewater that is significantly transformed in the environment prior to reaching the drinking water intake, while the analysis that included only the closest WWTPs (within 50 km) may have neglected wastewater that is reaching the intake after relatively little transformation. Figure 3.3 is a scatterplot showing the NDMA measures relative to fraction of nitrification (left panel) and nitrogen treatment (right panel) for the 150km cutoff. Plots of the results of the 50km, 100km, and unconfined analysis can be found in Figures B.3, B.4, and B.5, respectively.

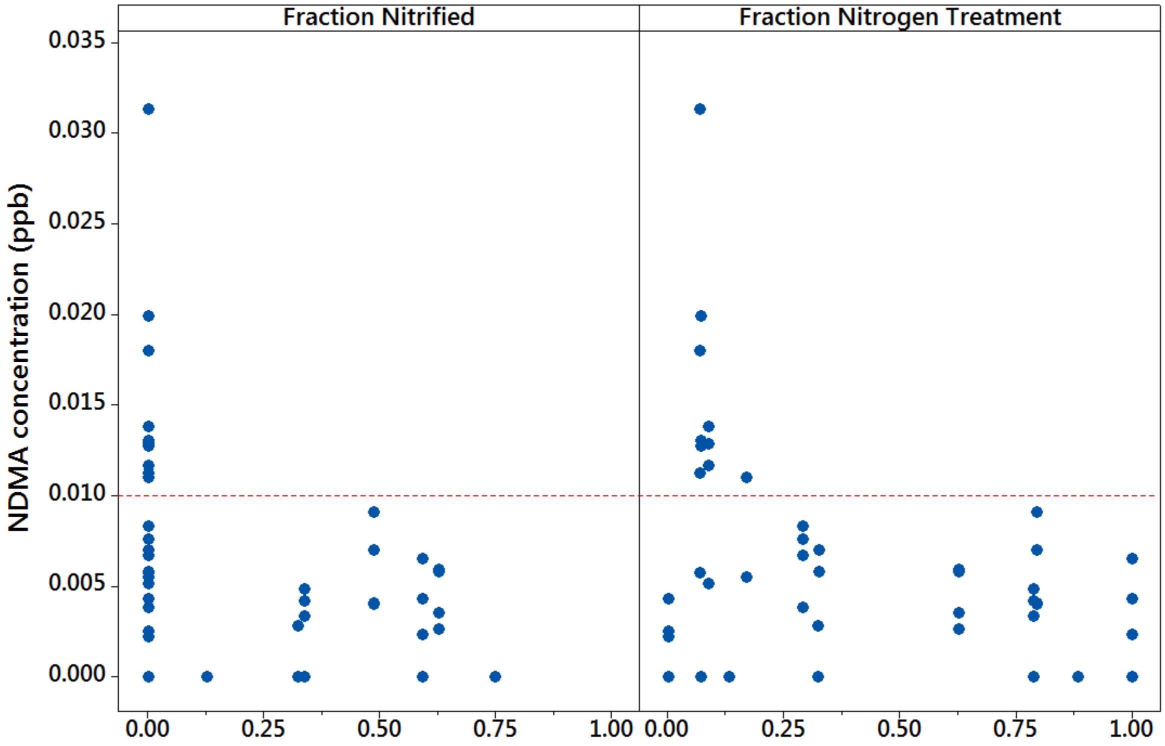


Figure 3.3. NDMA concentrations for chloraminating drinking water plants with upstream wastewater treatment facilities within 150 km, based on fraction of wastewater flows that are treated by nitrification (left) or include any nitrogen treatment (right). The horizontal red dashed line represents the California notification level of 10 ng/L.

All NDMA measures exceeding 10 ng/L occurred at chloraminating drinking water plants where upstream DFR was either not nitrified at all or had very low nitrification (fraction <0.001) (left panel). This is also seen for chlorinating plants; 4 detects observed in the high DFR chlorinating plants all occurred at a nitrification fraction of less than 0.02 (Figure B.6). Considering both extents of nitrogen treatment, which include those nitrifying treatment as well as treatment including nitrification and denitrification, NDMA concentrations above 10 ng/L are observed when a small fraction of nitrogen treatment occurs (<0.20) (Figure 3.3, right panel). This may suggest denitrification returns NDMA precursors to treated wastewater, as previously observed (Krasner et al., 2009a); however, the paucity of data in the low fraction of nitrification (between 0.001 and 0.2 in the left panel) precludes any comparative conclusion.

Influence of nitrification on DWTP NDMA formation

To further explore the relationship between upstream nitrification and DWTP NDMA formation, the median percent nitrification treatment for upstream wastewater effluent was used to split the NDMA data into low and high nitrification groups (except for in the 50km analysis). In the 50km analysis, 57% of the data had 0% upstream nitrification. In this case, all 0% nitrification data were grouped as low nitrification. For the 150km analysis, the split occurred such that the highest fraction of nitrification in the low nitrification group was 0.06% while the lowest nitrification in the high nitrification was 12.5% of upstream WW effluent discharges. In the 50km and 100km analyses, all plants in the low nitrification bin had 0% nitrification while all plants in the high nitrification had at least 10% nitrification. The empirical distributions for the grouped data in the 150km analysis are shown in Figure 3.4.

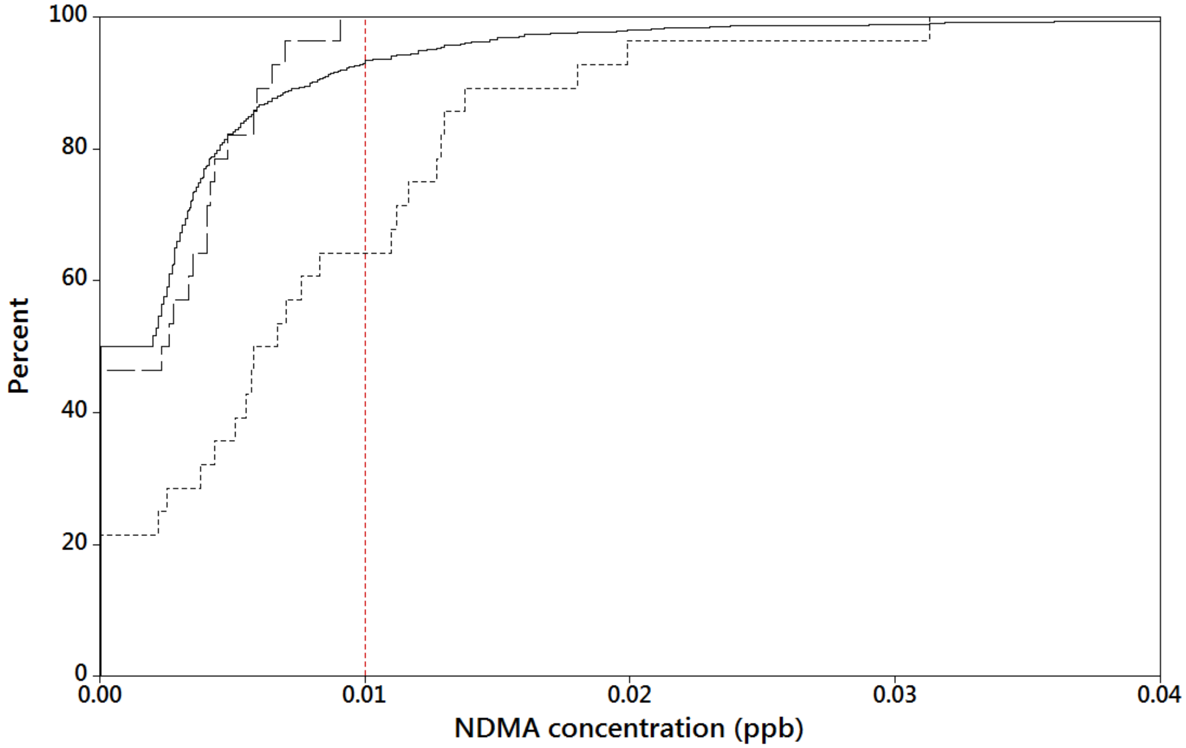


Figure 3.4. Empirical CDFs for the UCMR2 data (solid black) and the high nitrification (long dash) and low nitrification (dotted) in DFR data sets (as determined in the 150km analysis); only chloraminating plants are shown. The vertical red dashed line represents the California notification level of 10 ng/L.

The CDF of samples taken in the high nitrification group closely follows that of the UCMR2, with no significant difference observed between distributions of the UCMR2 and the high nitrification plants. However, the low nitrification group was significantly different (right shifted, higher NDMA) compared to the UCMR2. This pattern was also seen for the 50km and 100km radii analyses, but was not seen in the unconfined analysis (Figures B.7, B.8, and B.9). NDMA was more frequently detected in the low nitrification group than the high nitrification group for the 50km (low nit 69%, high nit 62%), 100km (low nit 79%, high nit 54%), and 150km (low nit

79%, high nit 54%) analyses. This difference was significant for the 100km and 150km analyses (p=0.041), but not for the 50km analysis (p=0.626).

The median NDMA detection in the low nitrification group was significantly higher than in the high nitrification group for the 50km, 100km, and 150km analyses (low nit 8.0 ng/L, high nit 4.2 ng/L, p=0.003 for each). In the 150 km analysis, about 36% of the samples for drinking water plants where upstream nitrification was low exceeded the California Division of Drinking Water's notification level of 10 ng/L NDMA (31% and 36% for 50km and 100km, respectively). This threshold was not exceeded for any drinking water plant where upstream wastewater treatment had high nitrification.

As noted previously, the high DFR plant set had a higher NDMA detection rate and higher NDMA concentrations reported than the overall UCMR. Dividing the high DFR drinking water plants into those with upstream wastewater plants practicing high and low nitrification shows that upstream nitrification led to high DFR drinking water plants that looked more similar to all drinking water plants (in the UCMR2) in terms of NDMA formation. However, high DFR drinking water plants with low rates of nitrification at wastewater plants upstream had much higher detection rates (nearly 80%) and elevated NDMA measurements. Thus, when DFR rates are high, nitrification at the upstream wastewater plants reduces NDMA formation at downstream drinking water plants affected by DFR. Thus, nitrification may be a valuable tool for mitigating NDMA formation at chloraminating DWTPs using wastewater-impacted source water.

Chapter 4 Incorporating Uncertainty into Future Estimates of Nitrous Oxide Emissions from Wastewater Treatment[1]

Abstract

Nitrous oxide (N_2O) is a potent greenhouse gas. Wastewater treatment is considered to be a minor source of N_2O; however, observed in-plant emission factors are more variable than previously considered. Further, emissions associated with treated wastewater effluent are highly uncertain. A model incorporating these uncertainties was compared with current N_2O estimates. The modified model features distribution-based emission factors and Monte Carlo simulation. Results of these simulations indicate N_2O emissions 7.3, 8.6, and 9.4 times estimates generated with the current method for in-plant, effluent-derived, and total emissions, respectively. Future changes in biological nutrient removal (BNR) associated with clean water objectives may alter N_2O releases. The model, which distinguishes between BNR and non-BNR treatment, predicts decreasing N_2O emissions with increasing BNR treatment. Examining the Chesapeake Bay system, the model suggests 2012 BNR levels reduced N_2O emissions by 0.86 MMT CO_2 eq per year and planned BNR expansions will result in emissions reduced by 1.77 MMT CO_2 eq relative to 0% BNR scenarios. The new estimation method would be improved through additional collection of data on effluent emissions.

Introduction

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[1] The contents of this chapter have been published as: Cadwallader, A., & VanBriesen, J. M. (2017). Incorporating Uncertainty into Future Estimates of Nitrous Oxide Emissions from Wastewater Treatment. *Journal of Environmental Engineering, 143*(8), 04017029. doi:10.1061/(ASCE)EE.1943-7870.0001231

Nitrous oxide is a major contributor to ozone depletion and climate change. It is currently the most abundant anthropogenic ozone-depleting emission, and is anticipated to remain so for the twenty-first century (Ravishankara et al., 2009). It is also the third most abundant greenhouse gas, after carbon dioxide and methane. N_2O accounts for only 0.02% of the mass emissions of the three most abundant greenhouse gases; however, its global warming potential is roughly 300 times that of CO_2. N_2O contributes about 6% to all greenhouse gas emissions within the United States (in CO_2 equivalents) (USEPA, 2014). Thus, N_2O's contribution to climate change is very high relative to its emission rate, and even small emission sources should be assessed. Agriculture, industrial acid production, and combustion are considered the largest anthropogenic contributors to nitrous oxide emissions within the United States (USEPA, 2014). The next largest anthropogenic source of nitrous oxide emissions is wastewater treatment. The U.S. Environmental Protection Agency (U.S. EPA) estimated emissions for these anthropogenic sources in the year 2008 are shown in Table 4.1. N_2O emissions from wastewater treatment for the year 2008 were considered to account for less than 1.2% of all nitrous oxide emissions in the Unites States; however, this assessment is based on a number of estimated values.

Table 4.1. Top anthropogenic N_2O sources in the United States for the year 2008 (Data from USEPA 2014)

Source	**N_2O Contribution (MMT CO_2 eq)**
Agricultural Soil Management	316
Mobile Combustion	25.5
Stationary Combustion	21.1
Manure Management	17.8
Nitric Acid Production	16.9
Wastewater Treatment	4.8
Adipic Acid Production	2.6

Wastewater treatment utilizes microbial processes to transform carbonaceous and nitrogenous materials in human, industrial, and commercial waste to microbial biomass, which is then settled out of the water. Several nitrogen transformations can take place in wastewater treatment plants, including nitrification (conversion of ammonia to nitrate) and denitrification (conversion of nitrate to nitrogen gas). Wastewater treatment plants providing conventional secondary treatment are designed to remove biological oxygen demand, and little nitrogen conversion takes place. Some treatment plants extend the solids retention time (or sludge age) to enable nitrification in conventional systems. Other treatment plants include both an aerated nitrification stage and an anoxic treatment step to enable denitrification for full biological nitrogen removal (BNR); the objective of this process is to transform influent ammonia to nitrogen gas, which is released to the atmosphere.

Nitrous oxide is a byproduct of nitrification and an intermediate in denitrification (Ni et al., 2013; Kampschreur et al., 2009). N_2O emissions have been observed from treatment plants even when nitrogen transformations are not intended (Czepiel et al., 1995), and emissions can come from multiple points within the treatment process (see Figure 4.1). Czepiel et al.(1995), for example, observed N_2O emissions primarily from aerated conventional secondary treatment tanks . N_2O emissions are generally greater from aerated zones of treatment processes than unaerated zones; however, high variability is reported both between plants and within the same plant (Rodriguez-Caballero et al., 2014; Foley et al., 2011; Ahn et al., 2010). The need for additional research into these highly variable emissions has been apparent for some time (Barton and Atwater, 2002). Despite the observation that aerated processes, such as nitrification, tend to contribute more to N_2O emissions, the Intergovernmental Panel on Climate Change (IPCC, 2006) and EPA (2014) models assume that denitrification (unaerated) processes are the dominant source of N_2O release within a wastewater treatment plant. Operational parameters that contribute to N_2O emissions from within a treatment plant include dissolved oxygen and nitrite concentrations during nitrification and denitrification, as well as low carbon availability during denitrification (Kampschreur et al., 2009).

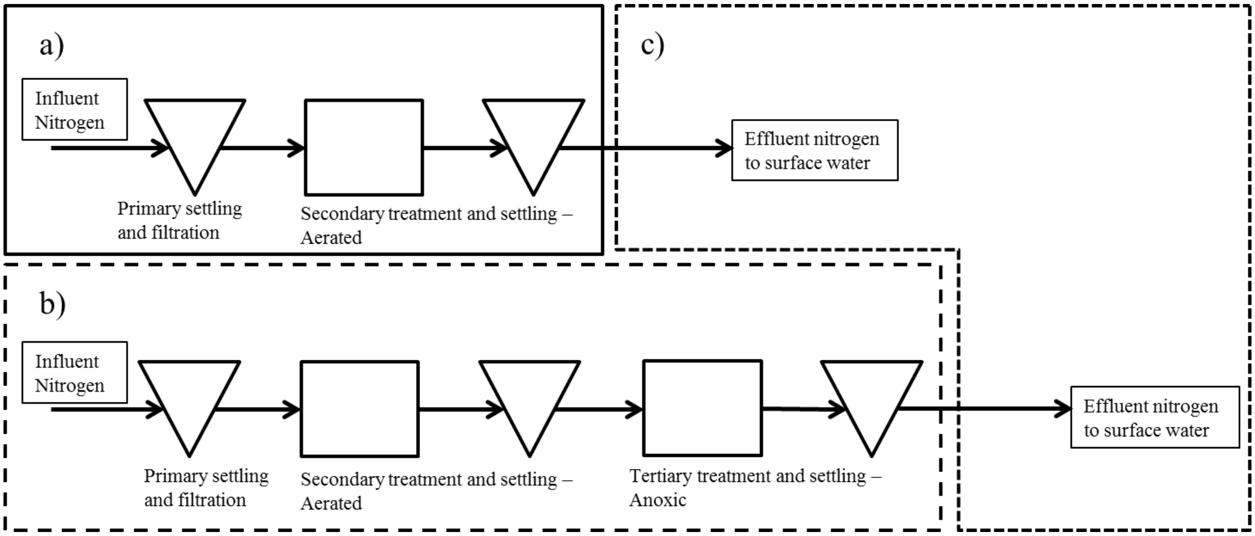

Figure 4.1. The three acknowledged categories of N2O emissions from wastewater treatment: a) non-BNR treatment plants that include primary and secondary treatment b) BNR treatment plants that include primary, secondary, and tertiary treatment c) effluent that has been discharged into the environment from wastewater treatment plants

BNR is increasingly deployed in wastewater treatment to fully remove nitrogen and reduce nutrient loading to receiving water bodies (Greening and Janicki, 2006). In response to increasing concerns about nutrient pollution causing harmful algal blooms and eutrophication in at-risk areas such as the Chesapeake Bay Watershed (Anderson et al., 2002; Boesch et al., 2001; Bowen and Valiela, 2001), BNR has been deployed successfully to improve water quality (Kemp et al., 2005; Boesch et al., 2001). BNR also has the potential to reduce total N_2O emissions from wastewater treatment (Wang et al., 2011). Further, a GHG crediting system for these emission reductions could offset up to 70% of the costs of operation and maintenance costs associated with BNR. Centralized BNR treatment is estimated to serve about 1.2% of the population in the United States (USEPA, 2014); thus, there is significant potential to expand this treatment technology. While N_2O is an intermediate in biological denitrification, emission levels are variable based on operational conditions (Yoshida et al., 2014; Kampschreur et al., 2009).

In addition to 'in-plant' emissions from wastewater treatment, N_2O is emitted when the nitrogen that is released in the wastewater treatment plant effluent is transformed through natural processes. This effluent-derived N_2O is considered to be the larger source of N_2O emissions associated with wastewater treatment (USEPA, 2014; Kampschreur et al., 2009; IPCC, 2006). River conditions are favorable for nitrous oxide production (Cole and Caraco, 2001) and numerous studies have demonstrated that rivers dominated by wastewater effluent have higher N_2O saturation values (Liu et al., 2015; Yu et al., 2013; Beaulieu et al., 2010). However, data regarding effluent-derived N_2O emission is lacking (IPCC, 2006).

Since wastewater treatment has the potential to be a substantial contributor to greenhouse gas emissions, improved predictive models, accounting for uncertainty and data gaps, are needed. The objectives in the present work are to (1) update the current approach to estimating N_2O emissions from wastewater treatment with a Monte Carlo component to account for variability and uncertainty, (2) compare the results from this modified model with results from a replication of the current approach, and (3) use the modified model to predict how increases in the use of BNR treatment may influence N_2O emissions from wastewater treatment. This final objective is addressed through an analysis of hypothetical national shifts in BNR treatment as well as on a watershed scale analysis of the Chesapeake Bay Watershed based on predicted changes in BNR treatment.

Methods

Current Model

In the 2014 *Inventory of U.S. Greenhouse Gas Emissions and Sinks: 1990- 2012* (USEPA, 2014), henceforth *Inventory*, for the year 2008, wastewater treatment was estimated to contribute 4.8 million metric tons (MMT) of CO_2 equivalents of N_2O to the atmosphere. The current estimation model used by the EPA is based on the approach in the Intergovernmental Panel on Climate Change's (IPCC) *2006 Guidelines for National Greenhouse Gas Inventories* (IPCC, 2006), which divides N_2O into in-plant emissions and effluent emissions. The EPA model further divides in-plant emissions into those generated from BNR treatment (defined by the EPA as including nitrifying and denitrifying stages) plants, N_2O_{BNR}, and those generated from non-BNR (conventional and/or nitrifying) plants, $N_2O_{non\text{-}BNR}$. Equations 1 and 2 provide estimates for in-plant emissions while Equation 3 provides an estimate for emissions from effluent, using the current EPA model structure. Table 4.2 provides a list of definitions and values for each of the variables in these equations.

$$N_2O_{BNR} = Pop_{BNR} * EF_{BNR}\left(\frac{\frac{gN_2O}{PE}}{year}\right) * F_{IND-COM} \tag{1}$$

$$N_2O_{non-BNR} = (Pop_{WWTP} - Pop_{BNR}) * EF_{non-BNR}\left(\frac{\frac{gN_2O}{PE}}{year}\right) * F_{IND-COM} \tag{2}$$

$$N_2O_{Effluent} = (((Pop_{WWTP} - (0.9 * Pop_{BNR})) * P_{consumed} * F_{NPR} * F_{IND-COM} * F_{NON-CON}) - N_{sludge}) * EF_{Effluent}\,(g\ N_2O - N/g\ N\ sewage) * 44/28\,(g\ N_2O/g\ N) \tag{3}$$

Table 4.2. Parameters used in the current approach to estimating N_2O emissions from wastewater treatment.

Symbol	**Parameter**	**Value** [a]	**Units**
Pop_{WWTP}	United States population serviced by centralized wastewater treatment	*242,170,000*	People
Pop_{BNR}	United States population serviced by BNR wastewater treatment	*2,900,000*	People
EF_{BNR}	Nitrous oxide emission factor for BNR treatment	7	g N_2O/PE/year
$EF_{non\text{-}BNR}$	Nitrous oxide emission factor for non-BNR treatment	3.2	g N_2O/PE/year
$EF_{Effluent}$	Nitrous oxide emission factor for wastewater effluent	0.005	g N_2O-N/g N
$F_{IND\text{-}COM}$	Factor to account for indutrial and commercial N discharges	1.25	
$F_{NON\text{-}CON}$	Factor to account for non-consumed protein	1.4	
$P_{consumed}$	Annual per capita protein consumption	*31,300*	g protein/ person/year
F_{NPR}	Weight fraction of nitrogen in protein	0.16	
N_{sludge}	Mass of nitrogen removed in WWTP sludge nationally	*268.7×10^9*	g N/year
N/A	Fraction of nitrogen removed in BNR plants	0.9	
N/A	Mass ratio of nitrous oxide to nitrogen required to form	44/28	

Note: Italicized values indicate inputs that change yearly, the values shown are the values for the year 2008, taken from U.S. EPA (2014).

These estimates are based on a two-part analysis, including an assumed nitrogen load and an estimated emission factor. The in-plant nitrogen load is estimated as the amount of nitrogen generated by residential, commercial, and industrial human activities annually that is flowing into centralized treatment plants (BNR or non-BNR) nationally. The nitrogen load in the effluent is the mass of nitrogen leaving all wastewater treatment plants (BNR and non-BNR), nationally, for a given year. Emission factors (for BNR, non-BNR and effluent) are intended to represent the portion of influent or effluent nitrogen that is emitted as N_2O.

BNR and non-BNR emission estimates are based directly on population data from the U.S. Census Bureau (US Census Bureau, 2013). The emission factors have units of mass nitrous oxide per population equivalent (PE) per year. The population served by centralized wastewater treatment is used to estimate a nitrogen load, which is then multiplied by a factor of 1.25 to account for industrial and commercial waste co-discharges of nitrogen to municipal wastewater treatment (Scheehle and Doorn, 2001; Tchobanoglous and Burton, 1991). This is then the total nitrogen assumed to be entering wastewater treatment.

The in-plant emission factors used for N_2O from non-BNR and BNR treatment are 3.2 and 7.0 g N_2O/PE/year, respectively (USEPA, 2014). The non-BNR value was estimated by Czepiel et al.(1995), based on a study of an activated sludge plant in Durham, New Hampshire. The BNR value was based on a study in Germany; however; the study plant demonstrated significant variability in N_2O emissions (Schön et al., 1993).

Nitrous oxide emissions from wastewater effluent are estimated with an emission factor with units of fraction of nitrogen mass flow. The nitrogen flow to effluent is calculated as all nitrogen flowing into treatment plants minus the amount of nitrogen removed in BNR (90% removal rate assumed (USEPA, 2014); and the amount removed in wasted sludge (NEBRA, 2007; USEPA, 1999). The total nitrogen load entering the plant is estimated using consumed protein estimates, $P_{consumed}$, taken from U.S. Department of Agriculture (US Department of Agriculture, 2012), as cited in the *Inventory* (USEPA, 2014), shown in Equation 3. An extra multiplier used for the effluent is a factor of 1.4 to account for non-consumed residential nitrogen (e.g., from garbage disposals, bathwater, and laundry (Scheehle and Doorn, 2001).

Once computed from the influent load and the assumptions of nitrogen removal in processing (through sludge disposal or BNR), the effluent nitrogen load is then multiplied by the effluent emission factor. The effluent emission factor, $EF_{Effluent}$, currently used is 0.005 g N_2O-N/g N in wastewater effluent, or 0.5% of the nitrogen in the wastewater effluent, and is taken directly from the IPCC guidelines (IPCC, 2006). This IPCC assumed emission factor was taken as 1% of nitrogen in the effluent prior to 2006 (Kampschreur et al., 2009). This emission factor is not based on observed data for effluent; it was calculated using components of EF_5, the emission factor for N_2O generated from runoff and leached nitrogen (IPCC, 2006). EF_5 consists of three components: EF_{5g}, EF_{5r}, and EF_{5e}, which originally came from Mosier et al. (1998). These components are N_2O emissions factors for nitrogen in groundwater/surface runoff, rivers, and estuaries, respectively (IPCC, 2006). Currently, EF_{5g}, EF_{5r}, and EF_{5e} are all assigned a value of 0.0025 as the fraction of nitrogen that is converted to N_2O in the respective system. These emission factors are considered additive, thus 0.75%, or 0.0075 as a mass fraction, of runoff nitrogen is expected to be emitted as N_2O as it makes its way to coastal waters. EF_5 represents this summation (IPCC, 2006). Since wastewater effluent has no leaching or running off phase, $EF_{Effluent}$ represents the summation of EF_{5r} and EF_{5e}. The value for EF_{5r} was reduced from 0.0075 to 0.0025 as a result of observed emission factors ranging from 0.03% to 0.05% in Dong et al. (2005) and Clough et al. (2006). The uncertainties provided for EF_5 and $EF_{Effluent}$ are the same, ranging from 0.0005 to 0.25, and stem from limited and highly variable data (IPCC, 2006).

Multiplying the net nitrogen load in effluent by the effluent emission factor yields a product in terms of mass of nitrogen, which is then converted to N_2O mass using stoichiometry. For all three of the components of N_2O emissions estimates from wastewater treatment, BNR plants, non-BNR plants, and effluent, the N_2O mass emissions can be converted to CO_2 equivalents by multiplying by a factor of 300.

Modified Model

The modified model proposed here makes several changes to the structure of the estimation method and updates data that are critical for the calculations. Table 4.3 summarizes the new variables in the modified model. First, rather than using separate equations for BNR and non-BNR emissions, a single equation with a weighted emission factor is used for in-plant emissions. This allows for high $Frac_{BNR}$ scenarios to be more easily examined with the model, since only $Frac_{BNR}$ has to be altered. N_2O emissions in-plant are computed as shown in Equation 4.

$$N_2O_{In-Plant} = EF_{weighted} * TKN \left(\frac{mg}{L}\right) * WW_{flow} \left(\frac{L}{yr}\right) * 44/28 \tag{4}$$

Where the weighted sum for the overall in-plant emission factor is calculated as shown in Equation 5.

$$EF_{weighted} = (Frac_{BNR} * EF_{BNR}) + ((1 - Frac_{BNR}) * EF_{non-BNR}) \tag{5}$$

Table 4.3. Additional parameters used in the modified approach to estimating N_2O emissions from wastewater treatment.

Symbol	**Parameter**	**Units**
TKN	Average concentration of TKN in wastewater	mg TKN/L
$EF_{weighted}$	Weighted sum of BNR and non-BNR emission factors	g N2O-N/g N
WW_{flow}	Annual wastewater flow in the United States	L
$Frac_{BNR}$	Fraction of wastewater treatment that includes BNR	

The annual fraction of treatment including BNR ($Frac_{BNR}$) can be varied in the model; however, in 2008 it was estimated to be about 1.2%.

In addition to incorporating a weighted emission factor, a different approach is also used for estimating nitrogen loading to wastewater systems in the United States. Rather than population and protein based assumptions, the Clean Watersheds Needs Survey (CWNS) (USEPA, 2012a) was used to estimate the total national wastewater flow (WW_{flow}); the 2008 value was 4.47×10^{13}L. The wastewater flow estimate is combined with an estimate of nitrogen concentrations in wastewater as total Kjeldahl nitrogen (TKN). The TKN estimate used in the following analysis was calculated using the EPA's estimate of total nitrogen flow for the year 2008 (extracted from Equation 3) and dividing by the national wastewater flow estimate (USEPA, 2012a). This value (about 48 mg TKN/L) is at the high end of reported ranges. As described in Scheehle and Doorn (2001), Tchobanoglous and Burton (1991) reports a range of 40-50 mg/L for residential wastewater while Mullick (cited in (Doorn et al., 1997)) reports a range of 20-50 mg/L. The Water Environment Federation (2011) reports an average range of 25-45 mg/L.

The equation for estimating emissions from wastewater effluent remains unchanged with the exception being that TKN and WW_{flow} are taken as the inputs for the estimate of nitrogen loading, as shown in Equation 6.

$$N_2O_{Effluent} = \left(\left(TKN * WW_{flow} \right) - \left(TKN * WW_{flow} * Frac_{BNR} * 0.9 \right) - N_{sludge} \right) * EF_{Effluent} * 44/28 \qquad (6)$$

In addition to changes in estimation equation structure, the modified model proposed here also differs in parameter input form for emission factors. This updated model uses a Monte Carlo method to simulate emissions estimates. A Monte Carlo approach was chosen because it enables for probabilistic simulations to be conducted when inputs are not adequately characterized for representative static values to be used. In this case, the uncertain inputs are the emission factors (Ahn et al., 2010; Foley et al., 2010; Kampschreur et al., 2009; IPCC, 2006). Rather than select single emission factors that may not be representative, distributions are fit to the available data. Then, following the Monte Carlo method, values are repeatedly sampled from those distributions for use in the model calculations. This generates multiple results, and the distribution of the results represents a most probable value as well as the uncertainty in the results due to the uncertain state of knowledge of the inputs. In-plant emission factors were set to distributions by pooling data from available literature and creating best fit distributions (see results below). Data specifically focusing on isolated effluent emission factors, however, were very limited and highly variable (IPCC, 2006). As a result, a distribution was created for the effluent emission factor using the IPCC uncertainty range (IPCC, 2006). Since this distribution was not created directly from pooled literature, simulations were also run using the currently used effluent emission factor of 0.5%.

Two scenarios were examined with the Monte Carlo model; both used in-plant emissions factors based on distributions of observations in published literature. Scenario 1 used the effluent emission factor that is assumed with the current model (0.005 g N_2O-N/g N) and thus isolates the effect of the in-plant emission factor variability on results. Scenario 2 used an effluent emission factor distribution fit based on the IPCC's (2006) listed uncertainty (this is discussed in the *Data Collection and Fitted Distribution* section). Each simulation consisted of one million iterations; each of which randomly sampled emission factors from the distributions and applied the emission equations (Equations 4, 5, and 6). Each iteration of a simulation generates an estimate for in-plant emissions ($N_2O_{\text{In-Plant}}$) and an effluent-derived emissions (N_2O_{Effluent}) using the provided equations. Results from the iterations within a simulation were plotted as cumulative probability. The median values of the simulation results were then used as point comparisons with results from replication of the current method. Additionally, the equivalent quantile (on the cumulative probability plot) of the current method estimate was examined.

The inputs used in one or both of the scenarios for in-plant emission factors and effluent emission factor, as well as the point value taken for TKN, are shown in Table 4.4. Details of the generation of the distributions are provided in Results and Discussion.

Table 4.4. Parameter distributions and point selections

Variable	Distribution[2]	Units for distribution
BNR Emission Factor	Weibull (0.76400, 1.44162)	% of N emitted as N2O
Non-BNR Emission Factor	Weibull (0.57661, 0.36936)	% of N emitted as N2O
Effluent Emission Factor	Weibull (1.07404, 6.03186) Point (0.5)	% of N emitted as N2O
TKN	Point Value (47.96)	mg/L

After generating results to compare with the emissions estimates using the current method for the year 2008, the conditions of scenario 2 (which included effluent emission factor uncertainty)

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[2] Weibull distributions continue infinitely, while % of N emitted as N_2O can only go up to 100%. Exceedance probabilities of 100% for the Weibull distributions were sufficiently low (BNR: $8.4\text{x}10^{-12}$, non-BNR: $1.1\text{x}10^{-11}$, effluent: $1.4\text{x}10^{-9}$) that this was considered negligible.

were used to examine how increases in BNR treatment frequency can be expected to alter N_2O emissions from wastewater treatment. Simulations were run for increasing values of $Frac_{BNR}$. $Frac_{BNR}$ values examined were 1.2%, 20%, 50%, 80%, and 100%. This demonstrates the general emissions trend predicted by this model for larger fractions of BNR treatment, which may eventually be required to reduce nutrient pollution associated with population growth and increased urbanization.

However, in order to examine an increase in BNR treatment, the N_{sludge} value in Equations 6 has to be altered as well. The assumption that 90% of nitrogen is removed in BNR treatment already includes the nitrogen removed as sludge. As BNR is increased, the 2008 estimate for N_{sludge} has to be proportionally decreased to prevent double-counting of removed nitrogen. For the BNR shift portion of the analysis, N_{sludge} is multiplied by the fraction of wastewater treatment that is non-BNR and the product effectively represents nitrogen removed in the sludge of non-BNR treatment plants. The result is Equation 7.

$$N_2O_{Effluent} = \Big((TKN * WW_{flow}) - (TKN * WW_{flow} * Frac_{BNR} * 0.9) - (N_{sludge} * (1 - Frac_{BNR})\Big) * EF_{Effluent} * 44/28 \tag{7}$$

This adjustment was negligible for 1.2% BNR treatment, since a relatively small mass of nitrogen is double counted. To verify this, differences between using the adjusted Equation 7 and Equation 6 were examined. Individual estimates differed by about 0.2% (not shown here). Thus, this adjustment was only necessary for the portion of the analysis intended to examine a BNR increase.

Shifting BNR in the Chesapeake Bay Watershed

The Chesapeake Bay Watershed is under significant regulatory pressure to manage nutrient loads through changes in management practices in agricultural regions and changes in operations at wastewater treatment plants in urban areas. Thus, this region has seen changes to wastewater biological nutrient removal and additional changes are anticipated in the future. The model developed in the present work was evaluated with a case example using the Chesapeake Bay Watershed. Existing and projected wastewater flow data were extracted from the 2012 Clean Watersheds Needs Survey (CWNS) (USEPA, 2016a). Data from the District of Colombia, Delaware, Maryland, New York, Pennsylvania, West Virginia, and Virginia were retrieved and filtered using hydrologic unit codes for areas within the Chesapeake Bay Watershed (US Geological Survey, 2014). A more in-depth discussion of the data handling is provided in Appendix C. Further, Table C.1 provides a list of the specific data tables used.

In addition to an increase in the fraction of wastewater treated with BNR, total wastewater flows within the Chesapeake Bay Watershed are projected to increase, from the 2012 existing flow of over 1800 mgd to the projected design capacity of over 2600 mgd. Thus, the model must consider projected N_2O emissions associated with process changes within the context of expected increases associated with additional wastewater flows (USEPA, 2016a). Anticipated changes in *both* the total wastewater flow and the fraction of BNR treatment are expected to influence total N_2O emissions. Because of this, multiple scenarios were created in which either one or both of these inputs were systematically varied. This approach was used to examine the isolated effects of wastewater flow increase and change in the fraction of BNR treatment as well as the combination of the two. Existing and projected conditions were used for wastewater flow. For the BNR treatment fraction, no BNR (0% of flow), the existing conditions (65% of flow), and projected conditions (81% of flow) were examined. In actuality, a third variable would be expected to change. Between the years 2000 and 2012, per capita annual wastewater flow decreased from 61,300 gallons to about 50,800 gallons. Thus, on a per person basis, less water is used to carry roughly the same amount of nitrogen and an elevated TKN concentration would be expected. However, here the TKN concentration of wastewater was kept consistent with the above national analysis at about 50 mg/L. TKN concentration was not varied in order to avoid obscuring the apparent influence of BNR treatment on N_2O emissions. However, it is possible that changing wastewater TKN concentrations may also alter fractional emission factors.

Results and Discussion

Data Collection and Fitted Distributions

A review of literature for in-plant emission factors produced a wide variety of emission factors for full-scale BNR and non-BNR treatment plants. Table 4.5 shows the data collected and used to fit distributions for BNR and non-BNR emission factors. Table C.2 lists individual data points. The formula for converting emission factor units is shown in Appendix C.3. The authors acknowledge that the measurement methods used to generate these values were widely variable. Once more published data becomes available additional data filtration can be afforded. However, the lack of data reduces the feasibility of high selectivity.

Table 4.5. Literature surveyed for in-plant emission factors

Source	**Treatment Type**	**Data Points**	**Values (% N emitted as N_2O)**
Sümer et al. (1995)	non-BNR	1	0.001
Czepiel et al. (1995)	non-BNR	1	0.035
Sommer et al. (1998)	non-BNR	1	0.02
Kampschreur et al. (2008)	BNR	1	4
Kampschreur et al. (2008)	non-BNR	1	2.3
Ahn et al. (2010)	BNR	10	0.01-1.6
Ahn et al. (2010)	non-BNR	9	0.03-1.8
Foley et al. (2010)	BNR	20	0.28-11.84
Weissenbacher et al. (2010)	BNR	1	1.3
Desloover et al. (2011)	BNR	2	5.1-6.6
Aboobakar et al. (2013)	non-BNR	1	0.036
Daelman et al. (2013)	BNR	1	2.8

These literature values for BNR and non-BNR emission factors were used to create best fit distributions. The resulting best fit distribution for BNR was Weibull (0.76400, 1.44162), and the best fit distribution for non-BNR was Weibull (0.57661, 0.36936). Figure 4.2 shows a cumulative probability plot of the available data (solid squares and diamonds), the matching best-fit distributions (solid lines), and the points where the best fit distribution is equivalent to the currently used emission factors (open shapes). The full range of reported data is shaded and boxed for BNR and non-BNR, respectively. Note that while the results are produced from simulations with one million iterations, figures were generated with ten thousand iteration simulations for practical purposes.

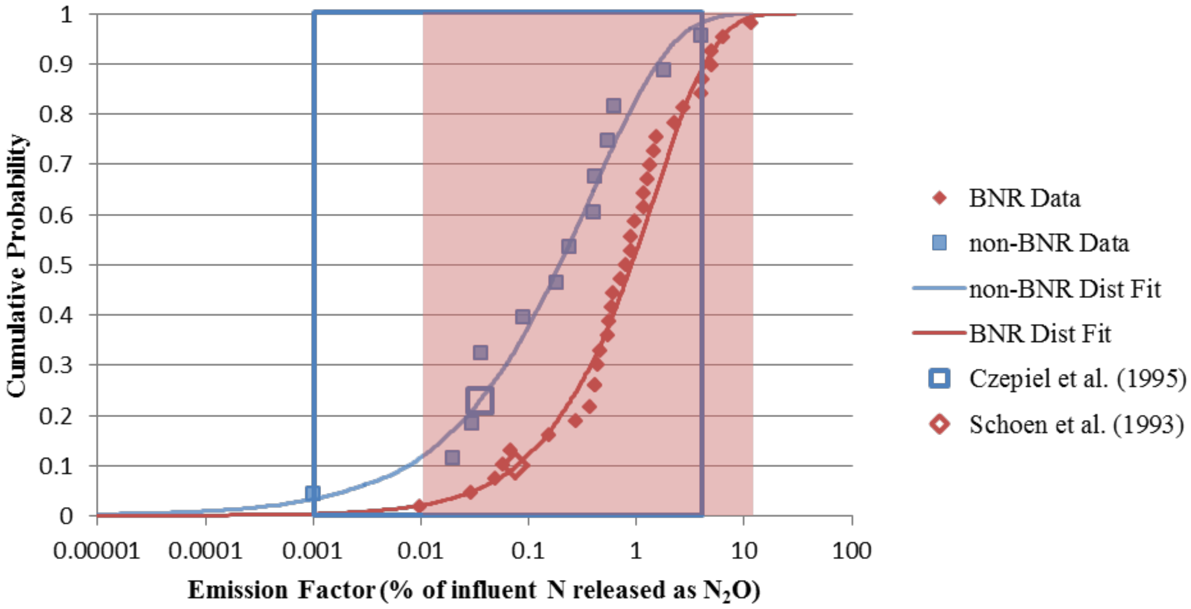

Figure 4.2. Cumulative probability plot of in-plant emission factors

Figure 4.2 shows that the current in-plant emission factor for non-BNR treatment is equivalent to the 23rd quantile of the fit distribution. The currently used BNR emission factor is equivalent to values at the 10th quantile of the best-fit distribution. Thus, the emission factors used for in-plant emissions estimates by the EPA are low relative to currently available data. Use of these factors is expected to result in underestimation of N_2O emissions from wastewater treatment. Figure 4.2 also demonstrates the significant overlap in reported values for non-BNR and BNR emission factors. The maximum value found in the literature for non-BNR emission factors is equivalent to the 88th quantile value of the best fit distribution for BNR emission factors, while the smallest observed emission factor for a BNR treatment plant was equivalent to the 12th percentile of the best fit distribution for non-BNR emission factors. The substantial overlap in the range of BNR and non-BNR emission factors suggests that categorizing plants as “BNR” or “non-BNR” may not be adequate to select an appropriate emission factor. Further, the selection of a single emission factor value for plants operating under different conditions may be problematic.

As noted above, the current effluent emission factor is also uncertain due to a lack of data (IPCC, 2006). Seitzinger and Kroeze (1998) predicted an emission factor of 1% from wastewater effluent, consistent with the value IPCC assumed (before its reduction to 0.5%). Beaulieu et al. (2011) estimated a threefold increase to the current EF_{5r} (0.0025 g N_2O-N/g N_2O). Turner et al. (2015) report an emission factor in a Minnesota river that was equivalent to 9 times the current EF_{5r}. And Liu et al. (2015) concluded that the current IPCC methodology underestimates N_2O emissions from urban rivers and lakes that receive high N loads. Thus, the reported emissions from wastewater effluent are highly variable, and a distribution was created to also represent the effluent emission factor. Since both in-plant emission factor distributions were best fit by Weibull distributions, Weibull was also selected for the effluent-derived emission factor distribution. Shape and location parameters were selected to set a value of 0.25 (the upper end of the IPCC's uncertainty range) to the 99th quantile and 0.005 (the IPCC and EPA's currently used effluent emission factor) to the mode of the distribution. The resulting distribution was Weibull (1.07404, 6.03186).

Current and Proposed Model Comparison

The new approach was used to generate results to compare with the current approach for estimating N_2O emissions from wastewater treatment and also generate results corresponding to gradually increasing fractions of BNR treatment ($Frac_{BNR}$). Scenario 1 uses distributions for only in-plant emission factors, while the effluent-derived emission factor is held to the same value it has in the EPA method. Scenario 2 incorporates the effluent-derived emission factor distribution in addition to the in-plant emission factor distribution.

Using the EPA method, in-plant emissions were estimated at 0.30 MMT CO_2 eq, while effluent-derived emissions were estimated at 4.4 MMT CO_2 eq for the year 2008; the sum is very close to the reported estimate of 4.8 MMT CO_2 eq (USEPA, 2014). The new approach is based on input distributions, and thus, the results generate a cumulative probability distribution. Figure 4.3 shows results of the new approach for scenario 2, where solid lines represent the cumulative probability plot of results for the in-plant, effluent-derived, and total emissions. The median (50 percentile) values are 2.18 MMT for in-plant, 37.4 MMT for effluent-derived, and 43.8 MMT for total emissions (note that while the means of the in-plant and effluent-derived emissions results are additive, medians are not). These values are significantly higher than the EPA-model-based values. Values for the EPA model are shown as vertical dashed lines in Figure 4.3 for comparison. The intersection of the dashed lines below the 50% cumulative probability on the solid lines indicates that the new approach predicts higher emissions than the EPA model. The EPA result is equivalent to the 13, 7, and 4 quantiles for in-plant, effluent-derived, and total emissions results, respectively.

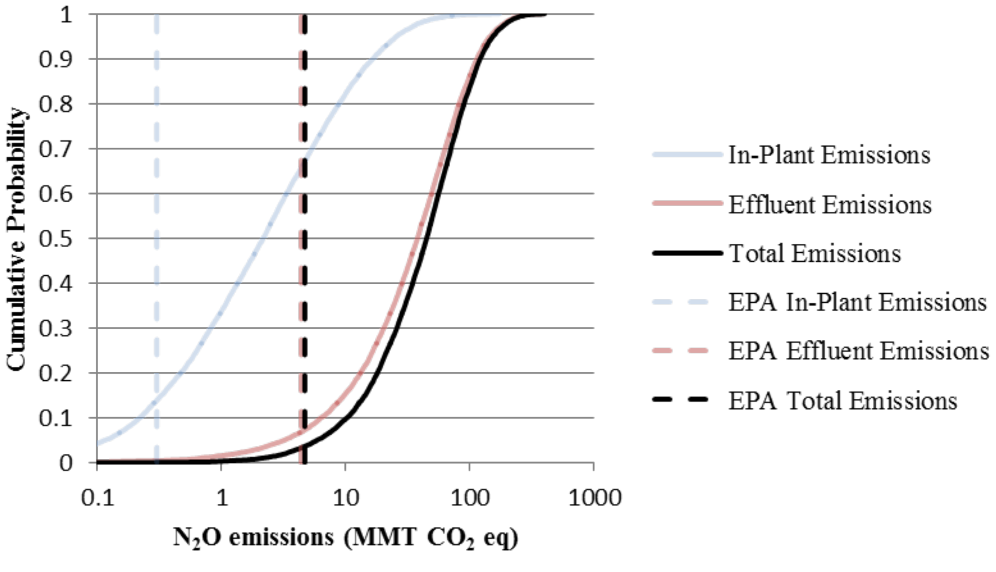

Figure 4.3. Probability based results for N2O emissions from wastewater treatment from scenario 2

Results for in-plant emissions and effluent-derived emissions for the two scenarios are shown in Table 4.6. In-plant emissions were independent of effluent emission factor; as a result, scenarios 1 and 2 had the same result for in-plant emissions. Data in Table 4.6 include the median, 90% confidence interval (Q5 to Q95), values generated with the current method, and the percentile on the cumulative probability plot of the current method estimate.

Table 4.6. Median in-plant and effluent emissions results, including 90% CI and cumulative probability at the current method estimate (all emissions in MMT CO_2 eq)

Emissions	Scenarios	Q5	Median	Q95	Value of Current Method Estimate	Quantile of Current Estimate
In-plant emissions	Scenario 1 & 2	0.118	2.18	24.93	0.3	13
Effluent emissions	Scenario 1	--	4.36	--	4.36	--
	Scenario 2	3.31	37.43	146.23		7

In-plant emissions for scenarios 1 and 2 had a median estimate of 2.18 MMT CO_2 eq; this is 7.3 times the estimate generated with the current EPA method. The estimate of 0.30 MMT CO_2 eq generated using the current method was equivalent to the 13th quantile. Thus, improved estimates of emission factors (based on available literature) significantly increases predictions of N_2O emissions from wastewater.

Table 4.6 also shows the results for effluent-derived emissions in each scenario. Scenario 1, which used the IPCC emission factor, produced the same result as the current method, as expected. Scenario 2 incorporated the effluent-derived emission factor uncertainty and demonstrates a substantial increase in emissions estimates. The median effluent-derived emissions estimate for scenario 2 was 37.4 MMT CO_2 eq, 8.6 times the estimate generated using the current approach. The estimate generated with the current method is equivalent to the 7th quantile of scenario 2. These results indicate that uncertainty in the effluent emission factor may be responsible for significant underestimation in effluent-derived emissions estimates.

Predictions of total emissions of N_2O from the current method replication and scenarios 1 and 2 are shown in Figure 4.4. Scenario 2 resulted in a much higher median emission estimate and a much wider 90% confidence interval. The difference between the scenario 1 and 2 results is entirely attributable to the use of the effluent-derived emission factor distribution in place of the point value currently used (0.5%). The effluent-derived emission factor is generally considered to be roughly an order of magnitude greater than either in-plant emission factor. Incorporating the uncertainty associated with this emission factor, which spans nearly 3 orders of magnitude (0.05%-25%), dominates the results of scenario 2.

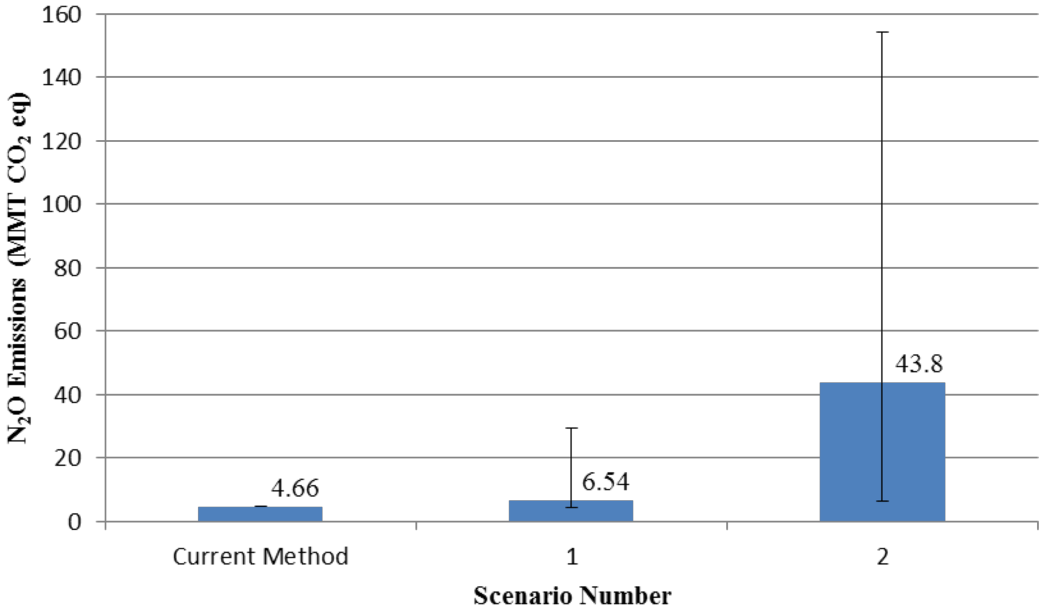

Figure 4.4. Total emissions median values for scenarios 1 and 2 compared to the current method estimate, with 90% confidence intervals

These distribution-based emission factor treatments (in-plant and effluent-derived) contributed to higher total emissions estimates in the model. Observed in-plant emissions factors reported in the literature are significantly higher than the assumed value in the EPA model. Scenario 1 produced a median total emissions estimate equivalent to 140% of the estimate generated for total emissions with the EPA approach. Scenario 2 produced a median total emissions estimate roughly 940% of the estimate generated with the EPA method.

If the median estimate for total emissions from scenario 2 were used in the EPA *Inventory* (2014) for the year 2008, N_2O emissions from wastewater treatment would be estimated as 43.8 MMT CO_2 eq, rising to be more important than mobile and stationary combustion (see Table 4.1) and the second highest source of anthropogenic N_2O. Emissions from wastewater treatment would rise from the 2008 estimate of 1.2% of all N_2O emissions in the United States to about 9.5% of all N_2O emissions.

Future BNR Implementation

Results for in-plant and effluent-derived N_2O emissions associated with increased BNR within U.S. treatment plants was evaluated by varying the fraction of BNR with the inputs of scenario 2. The fraction of wastewater treatment that includes BNR was examined at 1.2%,(used for the previous analysis) 20%, 50%, 80% and 100%. An increase in BNR would be expected to influence in-plant and effluent-derived emissions. The change to in-plant emissions is particularly difficult to assess because of the high degree of variability in reported N_2O emissions from different wastewater treatment plants (Table 4.5). Operational conditions have significant effect on N_2O emission levels, and the model does not account for such changes. Using reported N_2O emission factors for BNR and non-BNR plants leads to relatively small changes in modeled in-plant N_2O emissions as much of the range of values for BNR and non-BNR emission factors overlapped (see Figure 4.2). However, effluent emissions are expected to show significant change. Since BNR transforms influent nitrogen to nitrogen gas, effluent-derived nitrogen loads are expected to be much lower for BNR plants, leading to much lower effluent-derived emissions.

Changes in median in-plant and effluent-derived emissions, as well as the net change relative to the base case of 1.2% BNR, are shown in Figure 4.5 for different assumed BNR treatment fractions.

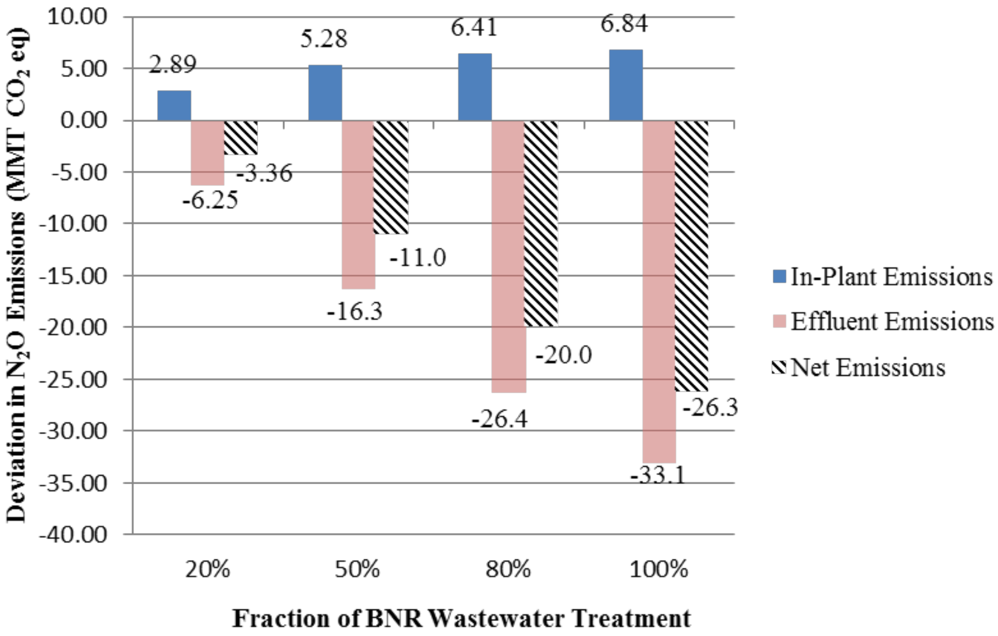

Figure 4.5. Median emission estimate changes relative to 1.2% BNR treatment

Figure 4.5 shows the effect of increasing BNR in wastewater treatment; in-plant and effluent-derived emissions changes. In-plant emissions increase with increasing BNR treatment due to the higher emission factor for BNR plants. At 100% BNR, the median estimate of in-plant emissions increases to about 414% of the in-plant emissions estimate at 1.2% BNR, increasing from 2.18 MMT CO_2 eq to 9.02 MMT CO_2 eq. However, counteracting the increased emission from BNR treatment is a drop in effluent-derive emissions. Since the emission factor for the effluent is generally estimated to be substantially larger than the in-plant emission factor, increased BNR, which reduces the nitrogen present in the effluent, would be expected to decrease effluent-derived emissions to a greater extent than it would increase in-plant emissions. At 100% BNR, emissions from the effluent would be expected to decrease by 33.1 MMT CO_2 eq. A complete shift to BNR treatment thus, would result in a net change in median estimates for in-plant and effluent-based emissions of -26.3 MMT CO_2 eq from the 2008 estimate (based on 1.2% BNR). Figure 4.6 shows the cumulative probability plots for total emissions estimates.

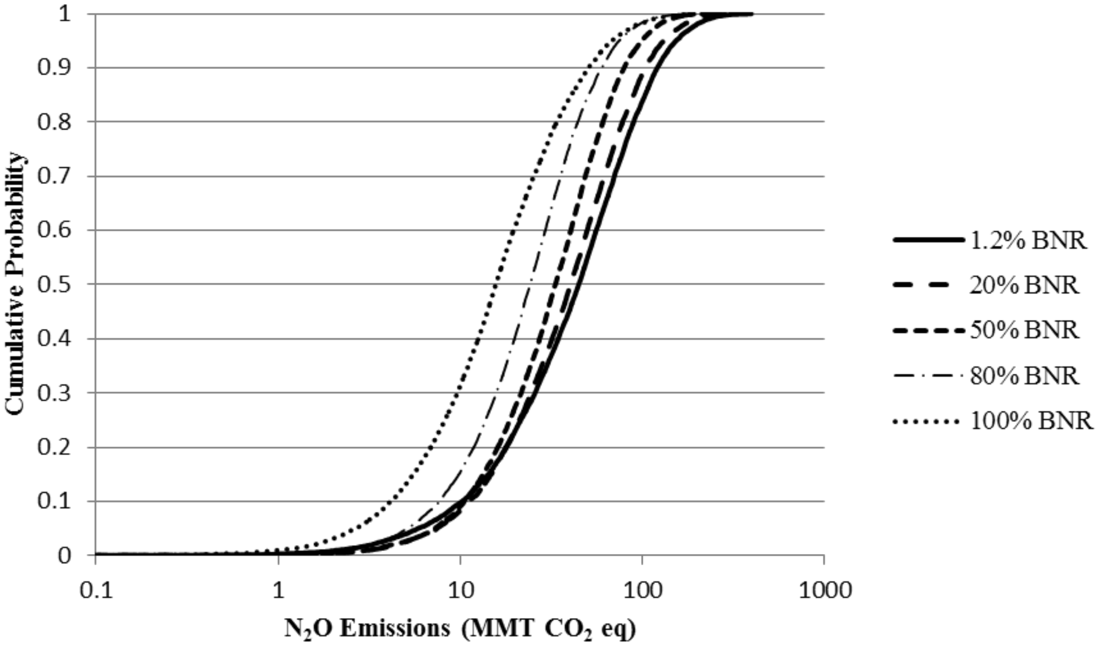

Figure 4.6. Total emissions of N_2O for gradually increasing fractions of BNR wastewater treatment

Figure 4.6 shows the leftward shift of cumulative probability plots with increasing BNR fractions, indicating decreased emissions as BNR increases. Median total emission estimates decreased from 43.8 MMT CO_2 eq at 1.2% BNR to 15.9 MMT CO_2 eq at 100% BNR. This trend is strongly influenced by the uncertainty of the effluent emission factor. Better informing this emission factor would provide improved estimates of the effect of BNR on U.S. N_2O emissions.

The modified model approach, which factors in diverse data for in-plant emission factors and the large uncertainty for effluent emission factors, produces considerably different results than the current EPA model. Median in-plant emissions were predicted to be 7.3 times the estimates generated using the current method, suggesting the EPA model should be updated to use more recent data on in-plant emissions factors. Effluent-derived emissions were also estimated to be much higher than the current approach indicates: 8.6 times the estimate for 2008 in the EPA *Inventory* (2014). Finally, median total emissions estimates were predicted to be 9.4 times greater than those generated with the current method. Emissions of this level from wastewater treatment would indicate that this sector accounts for 9.5% of U.S. N_2O emissions rather than the currently reported 1.2%. Given current emission factor data, increases in BNR wastewater treatment in response to increasing nutrient discharge control strategies would be expected to lower total N_2O emissions. This result depends on the highly uncertain effluent-derived emission factor. Indeed, the effluent-derived emissions factor represents the dominant uncertainty, and research to provide more accurate predictions of this value is needed.

Shifting BNR in the Chesapeake Bay Watershed

The Chesapeake Bay Watershed represents a region in which BNR treatment is likely to increase in the coming years to combat the negative effects of nutrient pollution on the Bay ecosystem. The present model was used to assess the effect of BNR on N_2O emissions. Reduced N_2O emissions from BNR may add a positive climate impact to the nutrient benefits. The total N_2O emission outputs for different BNR scenarios are summarized in Table 4.7. The resulting cumulative distributions are plotted in Figure C.1.

Table 4.7. Nitrous oxide emissions (as MMT CO_2 eq) in the Chesapeake Bay Watershed (5^{th}, 50^{th}, and 95^{th} quantiles)

Flow	BNR Percentage	Q5	Median	Q95
Existing	0%	0.35	2.52	8.90
	65%	0.36	1.66	4.84
	81%	0.29	1.36	4.17
Projected	0%	0.51	3.74	13.23
	65%	0.52	2.43	7.08
	81%	0.42	1.97	6.05

Table 4.7 provides the median value and 90% confidence interval for each scenario. Two trends are apparent within the table. For a given BNR percentage, higher emissions estimates are generated for the projected scenario. This is because of the anticipated increase in total wastewater nitrogen load from the expected increased population. Within a single flow condition, increasing fractions of BNR treatment result in decreased median emissions estimates. The model predicts this because the higher BNR fraction removes more nitrogen in-plant, where emission factors are low, while decreasing nitrogen released in the effluent that is subjected to transformation in the environment (where higher emission factors are observed). Based on these median values, the implementation of BNR treatment in the Chesapeake Bay Watershed (as of 2012) leads to 0.86 MMT CO_2 eq per year less than if no BNR were in the watershed. An additional 16% BNR (from 65 to 81% deployment) under 2012 flow conditions, would reduce nitrous oxide emissions by another 0.30 MMT CO_2 eq. This reduction is equivalent to the current estimated national in-plant emissions for 2008 and thus represents a significant mitigation potential. For projected flows, increasing BNR to the projected level (81%) is expected to lower N2O emissions by 1.77 MMT CO2 eq compared to no BNR and by 0.46 MMT CO2 eq compared to 2012 BNR levels (65%). This significant change is equivalent to just over 1% of the 2008 national emissions estimate for N_2O. Thus, the model predicts climate benefits from

increased BNR treatment in addition to the more commonly considered water quality improvements. BNR treatment in 2012 reduced emissions by about 34% while projected BNR treatment will reduce emissions by an additional 13% relative to their 0% BNR counterparts.

Conclusions

This research indicates that the use of static emission factors to represent BNR and non-BNR treatment trains represents an oversimplification of the difference in N_2O emissions from each of these categories. Further, the currently used emission factors are small relative to the data available in published literature for full-scale treatment plants (the 10th and 23rd percentiles for BNR and non-BNR emission factor distribution fits). Using data retrieved from a wide variety of sources for emission factors to estimate national emissions resulted in median estimates more than nine-fold greater than estimates generated with the current method. Finally, given the differences between in-plant and effluent-derived emission factors, increased levels of BNR treatment are expected to reduce total N_2O emissions in addition to improving water quality. This was demonstrated using the planned changes to wastewater treatment in the Chesapeake Bay Watershed as a case example. This approach to estimating N_2O emissions from wastewater treatment can be greatly enhanced through further emissions data collection both in-plant and downstream of plant discharge points, which will clarify the relationship between in-plant emissions and effluent-derived emissions. Specifically, attempts to estimate N_2O emission factors for effluent-discharged nitrogen would be valuable. Work dedicated to isolating plant-influenced N_2O emissions from effluent-receiving waterbodies would improve models. Within the treatment plant, research recording observed N_2O emission factors, as well as the treatment configurations they are associated with, would be very valuable for increasing the resolution at which large-scale N_2O emissions estimates could be generated. Increasing the available data pool would allow for the use of only data relevant to the area of focus when fitting emission factor distributions.

Chapter 5 Conclusions and Implications

The objective of this research was to examine the impacts of bromide and nitrogen discharged in wastewater effluent on downstream DWTPs, where these contaminants can influence the formation of DBPs. In the case of nitrogen, which may be biologically transformed or removed prior to reaching a downstream DWTP, N_2O emissions related to WWTP treatment decisions were also considered. This dissertation demonstrated that both bromide and nitrogen discharges affect downstream DWTP finished water DBPs. Further, that nitrogen treatment at WWTPs may have a larger greenhouse gas emission impact than previously thought.

Conclusions

Chapter 2 demonstrated that in southwestern Pennsylvania, an area where surface waters are known to be impacted by high bromide fossil fuel extraction and utilization-related wastewaters, major drinking water systems have successfully reduced TTHM. However, there has not been a significant drop in the brominated species of TTHM that are generally considered to be of higher concern and possibly are correlated with higher risk. Species-specific approaches to risk assessment indicate that risk associated with THM species has not decreased significantly despite the declining TTHM.

Chapter 3 demonstrated that NDMA detection and concentrations were elevated at chloraminating DWTPs with high DFR relative to baseline levels. At these high DFR, chloraminating DWTPs, NDMA concentrations were inversely correlated with the fraction of upstream wastewater discharges that had been nitrified at the WWTP. When separated by extent of upstream nitrification, those with a low fraction of upstream nitrification had significantly higher NDMA detection frequencies and measured concentrations than were seen in the national UCMR2 data. The high DFR plants with high upstream nitrification were not significantly different from the UCMR2 plants. The distance of WWTPs from the DWTP intake played an important role in whether a relationship was observed between nitrogen treatment choices and NDMA concentrations.

Chapter 4 demonstrated that the range of uncertainty in N_2O emissions from domestic wastewater treatment was too great to be adequately captured in the current method of estimation. Modifying the approach to estimating these emissions to include this significant uncertainty resulted in estimates nearly an order of magnitude larger than those generated using the current approach. A second observation was that biological nitrogen removal (BNR) contributed to large reductions in N_2O emissions. Removing nitrogen in the wastewater treatment plant elevated in-plant emissions, but this was offset by a much larger reduction in N_2O generated from nitrogen released to surface waters in treated effluent.

In Chapters 2 and 3, the concentrations of examined DBPs at DWTPs with source water impacted by wastewater discharges were abnormally high relative to a representative set of DWTPs (southeastern PA plants in Chapter 2, UCMR2 plants in Chapter 3). In the case of

NDMA, however, these elevated concentrations were dependent upon the distance of WWTPs from the DWTPs, indicating in-river nitrogen transformations affect this impact. Chapter 4 demonstrated that N_2O emissions associated with transformations of WWTP nitrogen may be minimized by cycling nitrogen within the controlled environment of the treatment plant, rather than discharging it.

Implications

The findings presented in this work may prove important for future treatment plant design, planning, and economic analysis. Enhanced treatment at WWTPs or alternate disposal methods with higher costs may be at least partially offset by DBP and GHG related benefits.

This work demonstrated that, in southwestern PA, TTHM concentrations were reduced in the last 20 years through the reduction of chloroform. Brominated species concentrations were not significantly reduced. While DWTPs are meeting the current TTHM regulation, the regulation may not be sufficient for control of more concerning DBP species. Metrics specifically focusing on brominated DBPs might be more effective at protecting human health.

This work also observed the increased NDMA formation associated with high DFR DWTPs. Nitrification at WWTPs appeared to have an added benefit of mitigating these increases in NDMA formation at downstream DWTPs. WWTPs with downstream DWTPs may want to consider the potential reduction in NDMA formation in addition to the more common concern of surface water hypoxia when determining whether nitrifying treatment is appropriate and cost-effective. This benefit could be enhanced through communication and cooperation between WWTPs and DWTPs.

Wastewater treatment and discharge may also be a more significant contributor to greenhouse gas emissions than previously thought. Accordingly, the reduction in N_2O emissions associated with incorporation of nitrogen removal may be more valuable than currently considered. This added value should also be considered in evaluating the costs and benefits of nitrogen removal at WWTPs.

While complete nitrogen removal appears most beneficial for N_2O emission reduction, nitrification-only treatment appeared most beneficial to the reduction of NDMA formation at downstream DWTPs. Previous work has noted that complete nitrogen removal treatment produced effluent with higher NDMAFP than nitrifying-only treatment, but still less than conventional treatment (Krasner et al., 2009a). Context may determine whether to prioritize nitrification-only or full nitrogen removal treatment. In areas of high DFR, where environmental health concerns (e.g., eutrophication) have not already motivated complete nitrogen removal, WWTPs may want to consider the benefit nitrification would have on downstream drinking water quality. In areas where DWTPs are sufficiently far downstream from WWTPs, the N_2O-reducing potential of complete nitrogen removal may be more valuable. This is particularly true if surface water quality is being adversely impacted by nitrogen discharges, as the value of N_2O reduction may serve as a supplemental benefit to the more commonly considered surface water benefits of nitrogen removal.

Chapter 6 Future Work

The work presented in this dissertation demonstrated the impact of wastewater nitrogen and bromide discharges on DBPs formed at downstream DWTPs. Further research should focus on the implications of this work for human health and engineering decision making.

Southwestern Pennsylvania's elevated bromide concentrations in surface waters have resulted in more brominated THMs. This bromination may have extended to other DBP classes in southwestern Pennsylvania drinking waters as well as other areas with high source water bromide concentrations. Future research should examine non-THM DBP classes alongside THMs in areas of high bromide surface waters to determine whether more brominated THMs are indicative of more brominated DBPs in general.

Further study should examine a set of well-characterized, chloraminating DWTPs and sample nitrogen species (including NDMA) at the intake, after subsequent treatment stages, and at the maximum residence time in the distribution system. This would help to elucidate whether high or low NDMA is linked to the presence of oxidized (nitrified) rather than reduced species of nitrogen in the influent. Some treatment plants of particular interest are the three high DFR DWTPs discussed in Chapter 3 that had NDMA concentrations above 10 ng/L. These three treatment plants are located in close proximity on the Mississippi River. Additional chloraminating plants with high DFR but low NDMA should also be evaluated in the same manner. Assessing the differences in source water nitrogen will further understanding of the relationship between WWTP treatment and NDMA formation at downstream DWTPs.

Biological transformation of wastewater nitrogen, and where it occurs, plays a large role in determining the related N_2O emissions. However, a large degree of uncertainty remains around N_2O emissions from effluent discharge, as no studies of effluent-sourced N_2O emissions exist. Research quantifying N_2O emissions from wastewater effluent nitrogen would be important to improving these estimations. This would require extensive river monitoring, both upstream of the discharge point and downstream for nitrogen concentrations and N_2O release, following established methods (Beaulieu et al., 2010; Dong et al., 2005). Further, mass loading of nitrogen to the surface water via effluent discharge would need to be monitored. This work would improve understanding of the relationship between WWTP nitrogen treatment and N_2O release.

Future work should also evaluate the costs and benefits of the wastewater treatment and disposal decisions discussed in this dissertation. In the case of bromide, alternative disposal practices or additional treatment should be considered to prevent bromide discharges. While these practices may incur added cost, they may be offset by the value of reducing brominated DBPs for the population served by downstream DWTPs. This also applies to ammonia and nitrogen removal. The potential to reduce either downstream N-DBPs or total N_2O emissions may provide significant value to nitrogen treatment to supplement more typical surface water quality benefits associated with reduced eutrophication potential. Properly incentivized, these benefits may increase BNR at WWTPs in areas of high DFR, reducing nutrient impacts in the environment.

Appendix A. Temporal and Spatial Variability in Bromination of Pennsylvania Drinking Water Disinfection Byproducts

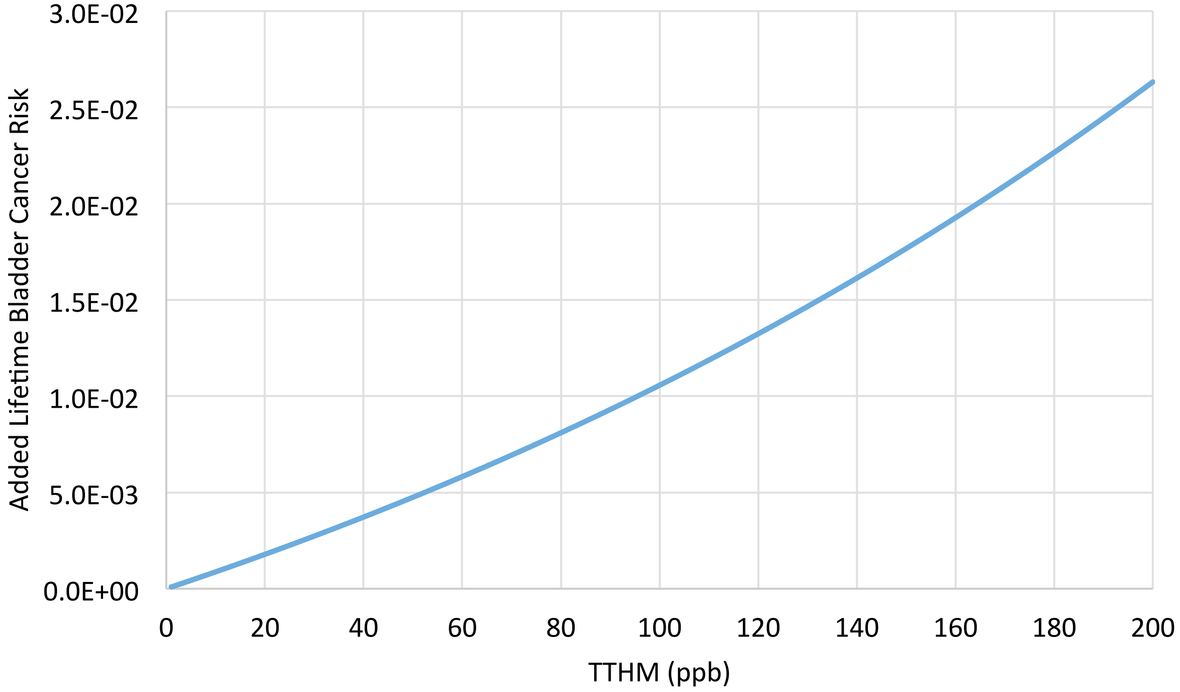

Figure A.1. Plot of the relationship between TTHM and added risk of bladder cancer as developed in Regli et al. (2015)

Appendix B. Impact of Nitrogen Removal in Wastewater Treatment on DBP Formation at Downstream Drinking Water Treatment Plants

B.1 High DFR DWTPs

Table B.1. System information for the 31 systems included in the high DFR system set

PWSID	Name	Plant Size	HUC 2	Source Water
AL0000933	ALBERTVILLE UTILITIES BOARD	L	6	Lake Guntersville
AL0001084	DECATUR (MUNICIPAL UTILITIES BOARD OF)	XL	6	Tennessee River
GA1210001	ATLANTA	XL	3W	Chattahoochee River
GA2150000	COLUMBUS	XL	3W	Chattahoochee River
IA8222001	**IOWA-AMERICAN WTR CO-DAVENPORT**	**XL**	**7**	**Mississippi River**
IL0894070	AURORA	XL	7	Fox River
IL0894380	ELGIN	XL	7	Fox River
IL1610450	**MOLINE**	**L**	**7**	**Mississippi River**
IL1610650	**ROCK ISLAND**	**L**	**7**	**Mississippi River**
IN5202020	FORT WAYNE - 3 RIVERS FILTRATION PLANT	XL	4	St. Joseph River
IN5282002	EVANSVILLE WATER UTILITY	XL	5	Ohio River
KY0110097	DANVILLE CITY WATER WORKS	VL	5	Herrington Lake
KY0370143	FRANKFORT PLANT BOARD	VL	5	Kentucky River
KY0730533	PADUCAH WATER WORKS	VL	5	Ohio River

NC0229025	DAVIDSON WATER INC	XL	3N	Yadkin River
NC0343045	HARNETT CO DEPT OF PUBLIC UTIL	XL	3N	Cape Fear River
NC0392020	CARY, TOWN OF	XL	3N	Jordan Lake
NJ1111001	TRENTON WATER WORKS	XL	2	Delaware River
NJ1225001	MIDDLESEX WATER COMPANY	XL	2	Delaware River
NY0100205	GUILDERLAND TOWN WD	L	2	Watervliet Reservoir
PA1090026	LOWER BUCKS CO JOINT MUN AUTH	XL	2	Delaware River
PA1460048	NORTH WALES WATER AUTHORITY	VL	2	Delaware River
PA5020043	WEST VIEW BORO MUNI AUTH	XL	5	Ohio River
PA5020056	WILKINSBURG-PENN JT WATER AUTH	XL	5	Allegheny River
SC0720003	BJW&SA (0720003)	VL	3N	Savannah River
TN0000107	TENN-AMERICAN WATER COMPANY	XL	6	Tennessee River
TN0000116	CLARKSVILLE WATER DEPARTMENT	XL	5	Cumberland River
TN0000286	HARPETH VALLEY U D	VL	5	Cumberland River
TN0000366	KNOXVILLE UTILITIES BOARD-KUB	XL	6	Tennessee River
TX0140005	CITY OF TEMPLE	VL	12	Leon River
TX0700001	CITY OF ENNIS	L	12	Lake Bardwell

Plants in bold had NDMA measurements consistently over 10 ng/L

Table B.2. Contributing WWTP count for each high DFR DWTP by analysis distance

PWSID	Unconfined	50km	100km	150km
AL0000933	2	2	2	2
AL0001084	164	11	22	28
GA1210001	11	4	6	11
GA2150000	29	5	11	16
IA8222001	767	23	54	108
IL0894070	45	15	36	45
IL0894380	37	22	34	37
IL1610450	766	22	53	104
IL1610650	766	22	53	107
IN5202020	18	7	18	18
IN5282002	1322	8	32	59
KY0110097	5	5	5	5
KY0370143	30	3	18	24
KY0730533	2032	9	30	73
NC0229025	13	5	13	13
NC0343045	25	7	20	25
NC0392020	2	2	2	2
NJ1111001	96	6	41	62
NJ1225001	24	24	24	24
NY0100205	4	4	4	4

PA1090026	105	15	45	70
PA1460048	94	16	54	65
PA5020043	310	65	161	252
PA5020056	159	25	85	116
SC0720003	46	1	3	7
TN0000107	132	2	13	38
TN0000116	62	5	14	20
TN0000286	54	5	12	22
TN0000366	60	11	20	39
TX0140005	16	4	7	10
TX0700001	2	2	2	2

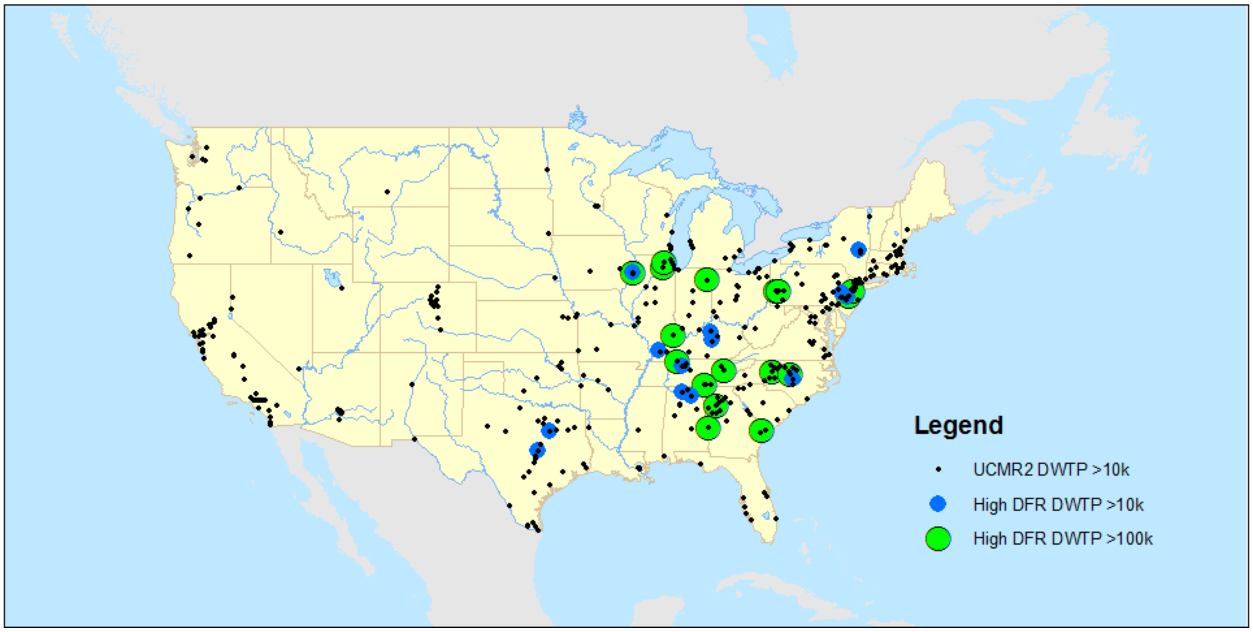

Figure B.1. DWTP locations for plants serving >10k people in the UCMR2 (black dots), high DFR plants serving >10k people (small blue circles), and high DFR plants serving >100k (large green circles)

B.2 High DFR DWTP NDMA Data

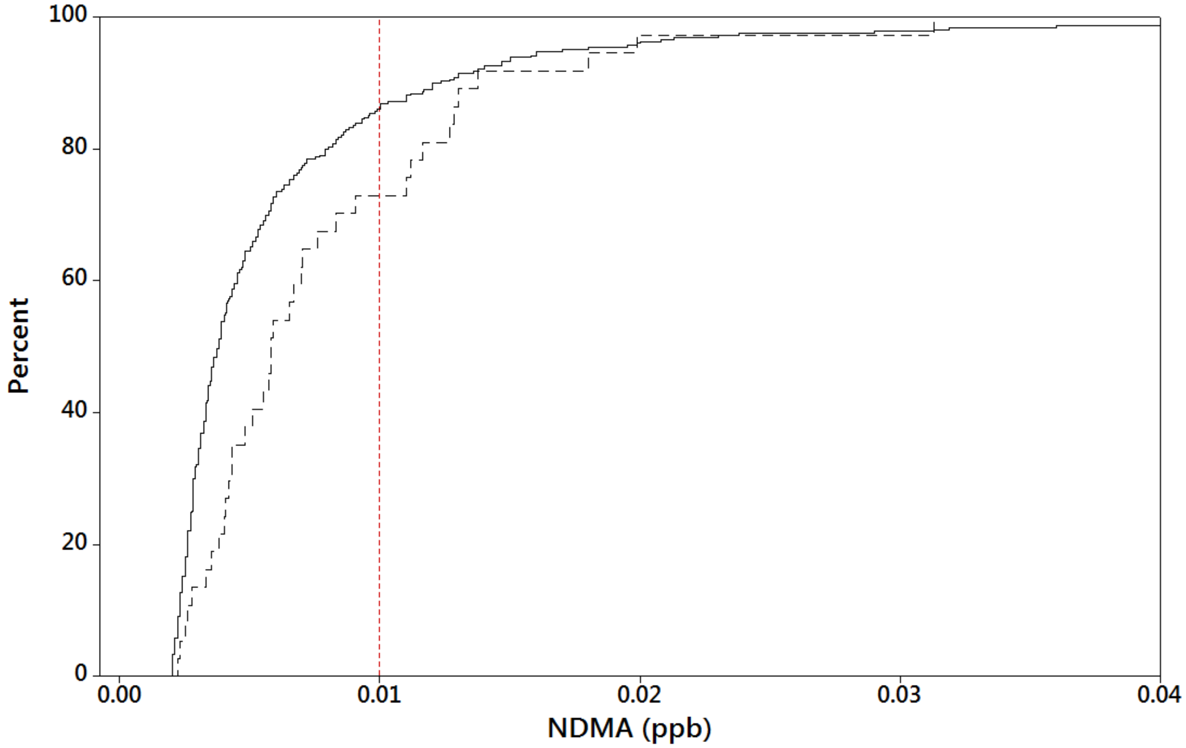

Figure B.2. Empirical CDF of NDMA detections at the maximum residence time for chloraminating plants for the UCMR2 (solid) and high DFR subset (dashed). The vertical dashed line marks the California notification level of 10 ng/L

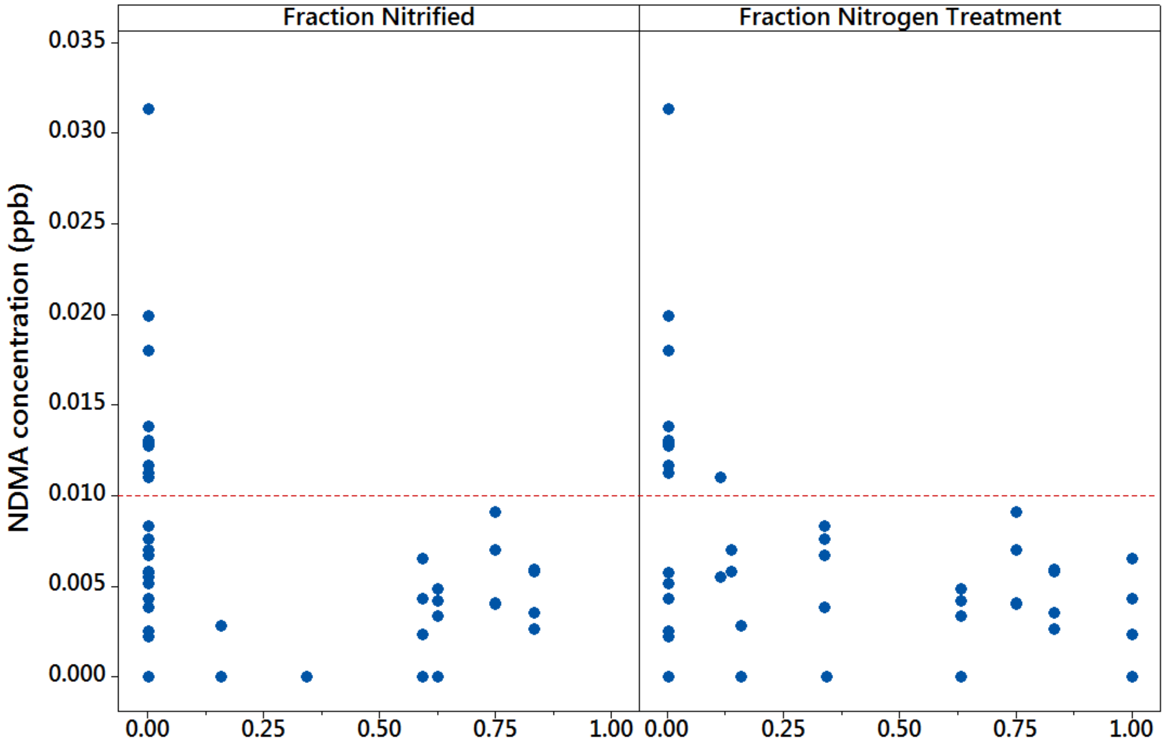

Figure B.3. NDMA concentrations for chloraminating drinking water plants with upstream wastewater treatment facilities within 50 km, based on fraction of wastewater flows that are treated by nitrification (left) or include any nitrogen treatment (right). The horizontal red dashed line represents the California notification level of 10 ng/L.

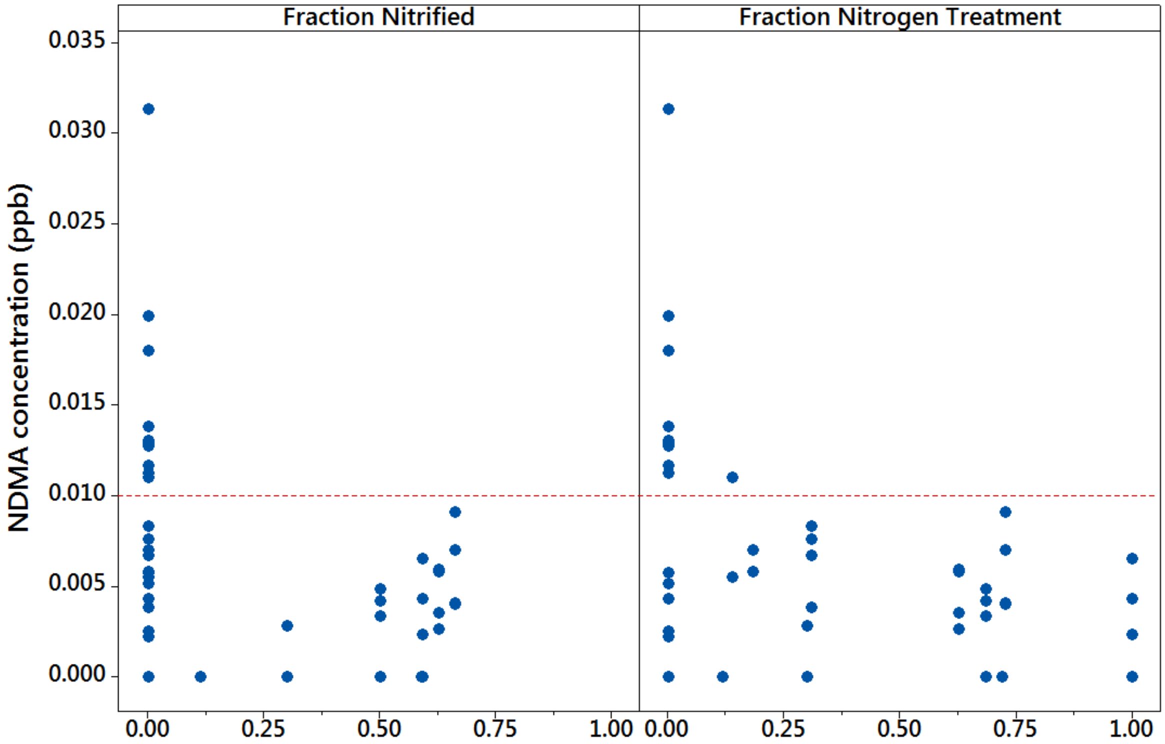

Figure B.4. NDMA concentrations for chloraminating drinking water plants with upstream wastewater treatment facilities within 100 km, based on fraction of wastewater flows that are treated by nitrification (left) or include any nitrogen treatment (right). The horizontal red dashed line represents the California notification level of 10 ng/L.

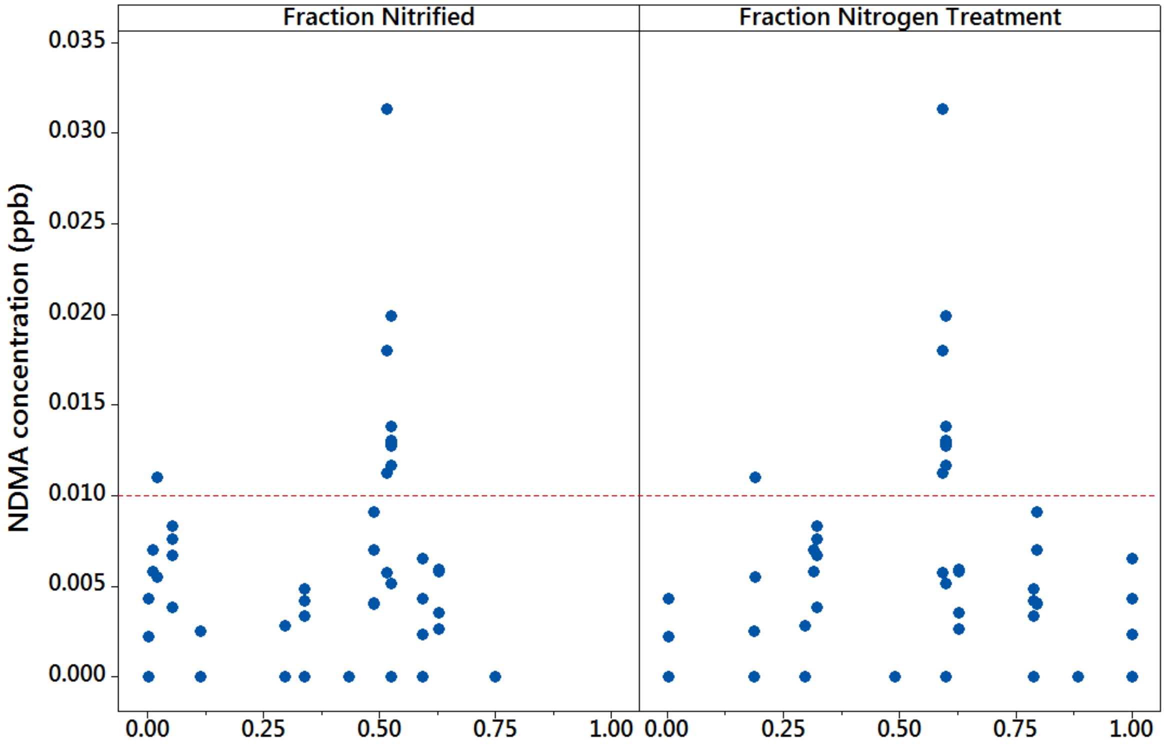

Figure B.5. NDMA concentrations for chloraminating drinking water plants with upstream wastewater treatment facilities, based on fraction of wastewater flows that are treated by nitrification (left) or include any nitrogen treatment (right). The horizontal red dashed line represents the California notification level of 10 ng/L.

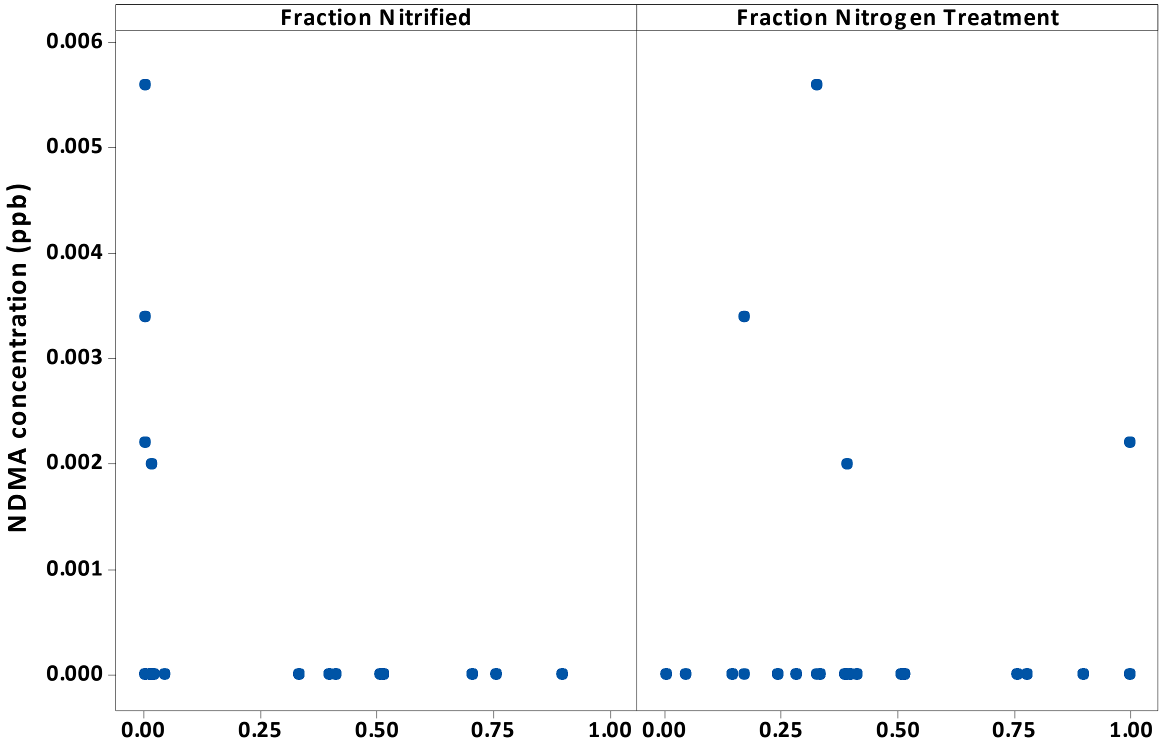

Figure B.6. NDMA concentrations for chlorinating drinking water plants with upstream wastewater treatment facilities within 150 km, based on fraction of wastewater flows that are treated by nitrification (left) or include any nitrogen treatment (right).

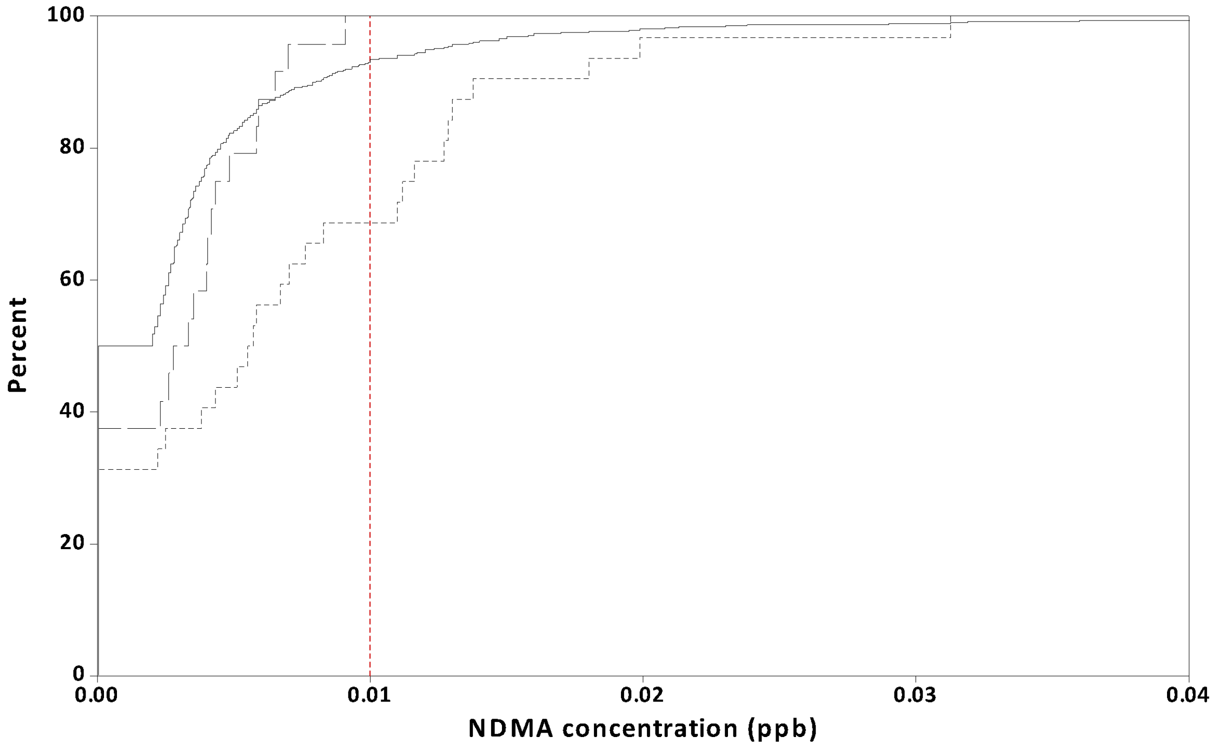

Figure B.7. Empirical CDFs for the UCMR2 data (solid black) and the high nitrification (long dash) and low nitrification (dotted) in DFR data sets (as determined in the 50km analysis); only chloraminating plants are shown. The vertical red dashed line represents the California notification level of 10 ng/L.

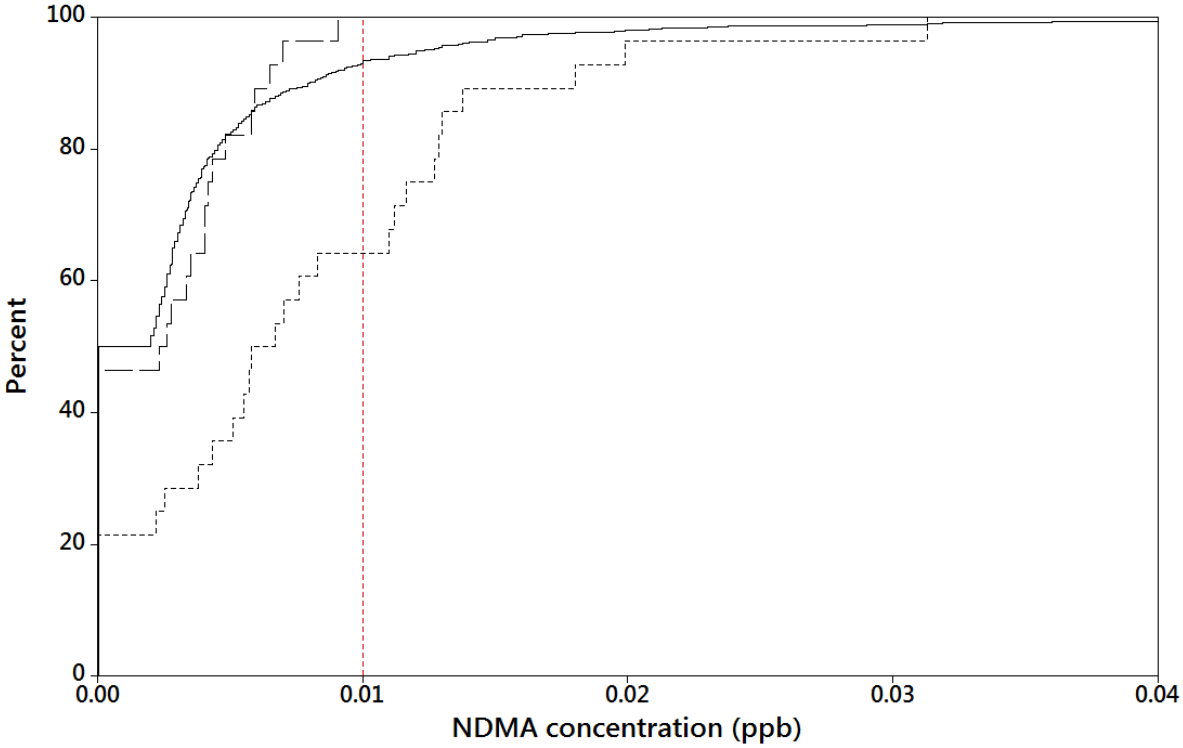

Figure B.8. Empirical CDFs for the UCMR2 data (solid black) and the high nitrification (long dash) and low nitrification (dotted) in DFR data sets (as determined in the 100km analysis); only chloraminating plants are shown. The vertical red dashed line represents the California notification level of 10 ng/L.

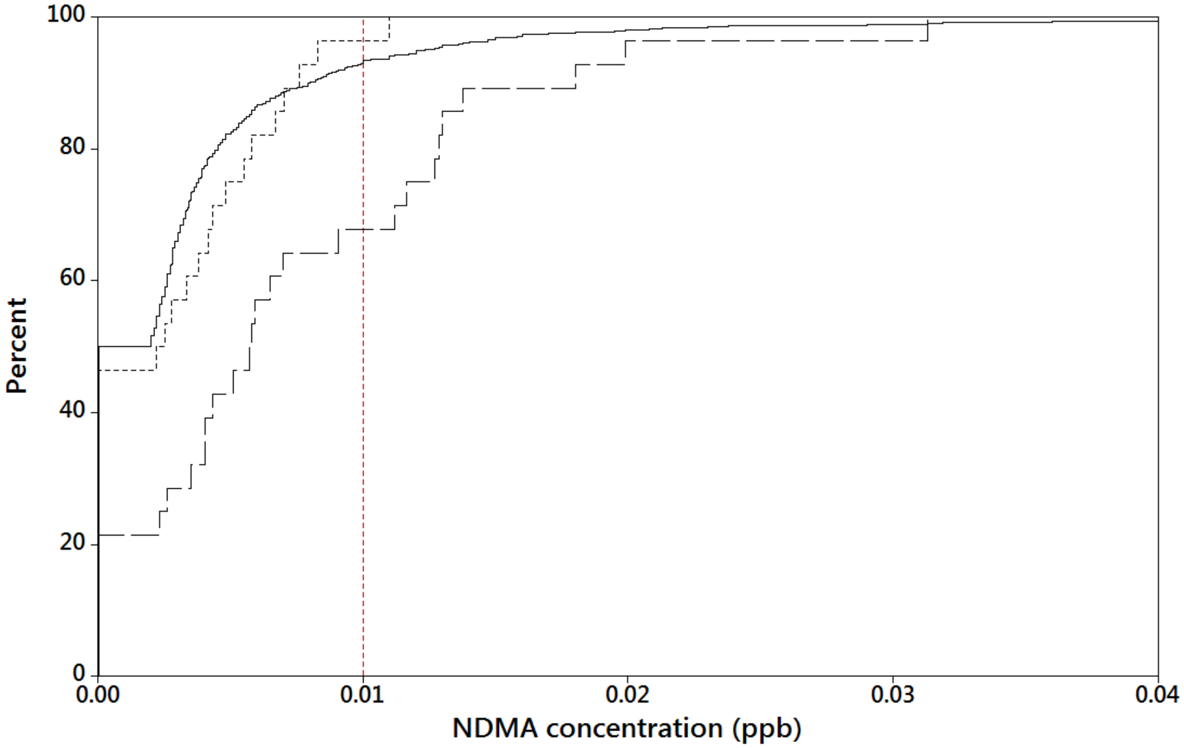

Figure B.9. Empirical CDFs for the UCMR2 data (solid black) and the high nitrification (long dash) and low nitrification (dotted) in DFR data sets (as determined in the unconfined analysis); only chloraminating plants are shown. The vertical red dashed line represents the California notification level of 10 ng/L.

Appendix C. Incorporating Uncertainty into Future Estimates of Nitrous Oxide Emissions from Wastewater Treatment

C.1 Data for the Chesapeake Bay Watershed

Relevant data were spread across a number of tables in the CWNS data set. Table C.1 shows the CWNS data table names and the corresponding fields that were extracted for the data analysis. All data entries were linked by the field CWNS_NUMBER, which served as an identification number for all facilities in the Clean Watersheds Needs Survey.

Wastewater infrastructure from the extracted list was filtered based on hydrologic unit code (HUC) number, which was available as a HUC8 in the field WATERSHED_HUC. For the Chesapeake Bay Watershed, HUC4 values of 0205, 0206, 0207, and 0208 were used (US Geological Survey, 2014). To narrow the results to only wastewater treatment plants, a filter was applied to the FACILITY_OVERALL_TYPE field to show only results for wastewater treatment, which removed other subcategories such as stormwater and decentralized wastewater treatment, and to the FACILITY_TYPE field to show results for only treatment plants, which filtered out infrastructure such as collection systems and biosolids handling facilities. After applying these filters, the remaining data entries represented all wastewater treatment plants present within the Chesapeake Bay Watershed included in the 2012 CWNS (USEPA, 2016a).

To determine the number of treatment plants in this data set that have nitrogen control technology currently or projected for the future, a count function was applied to

PRES_NITROGEN_REMOVAL and PROJ_NITROGEN_REMOVAL, which is a field with a positive input if the corresponding plant has nitrogen removal. To determine flows treated with nitrogen removal, for flow categories from the SUMMARY_FLOW data table (EXIST and PROJ), plant flows only for treatment plants that indicated nitrogen removal was conducted were summed. Note that EXIST flows indicate measured flows, and PROJ flows indicate projected design flows. These nitrogen removal only values were then compared to the full plant count and the total wastewater flow summations for current and projected scenarios. A few wastewater treatment plant entries discharge to other treatment plants, and some of these treatment plants count only their added flow while others counted both flows received from other plants and their own flows. This means that some treatment plants double counted flows. However, plants discharging to other plants had flows accounting for less than half of a percent of total wastewater flow in the Chesapeake Bay Watershed, so this effect was considered negligible in the current assessment. If applying these methods in other regional analyses, the double counting fraction should be determined to be small prior to interpretation of results.

Table C.1. CWNS data fields used for analysis

Data Table	**Field**
SUMMARY_FACILITY_TYPE	CWNS_NUMBER
	FACILITY_TYPE
	FACILITY_OVERALL_TYPE
SUMMARY_WATERSHED	WATERSHED_HUC
SUMMARY_EFFLUENT	PRES_NITROGEN_REMOVAL
	PROJ_NITROGEN_REMOVAL
SUMMARY_FLOW	EXIST_MUNICIPAL
	EXIST_INDUSTRIAL
	EXIST_TOTAL
	PROJ_MUNICIPAL
	PROJ_INDUSTRIAL
	PROJ_TOTAL

C.2 Chesapeake Bay Emissions Estimates

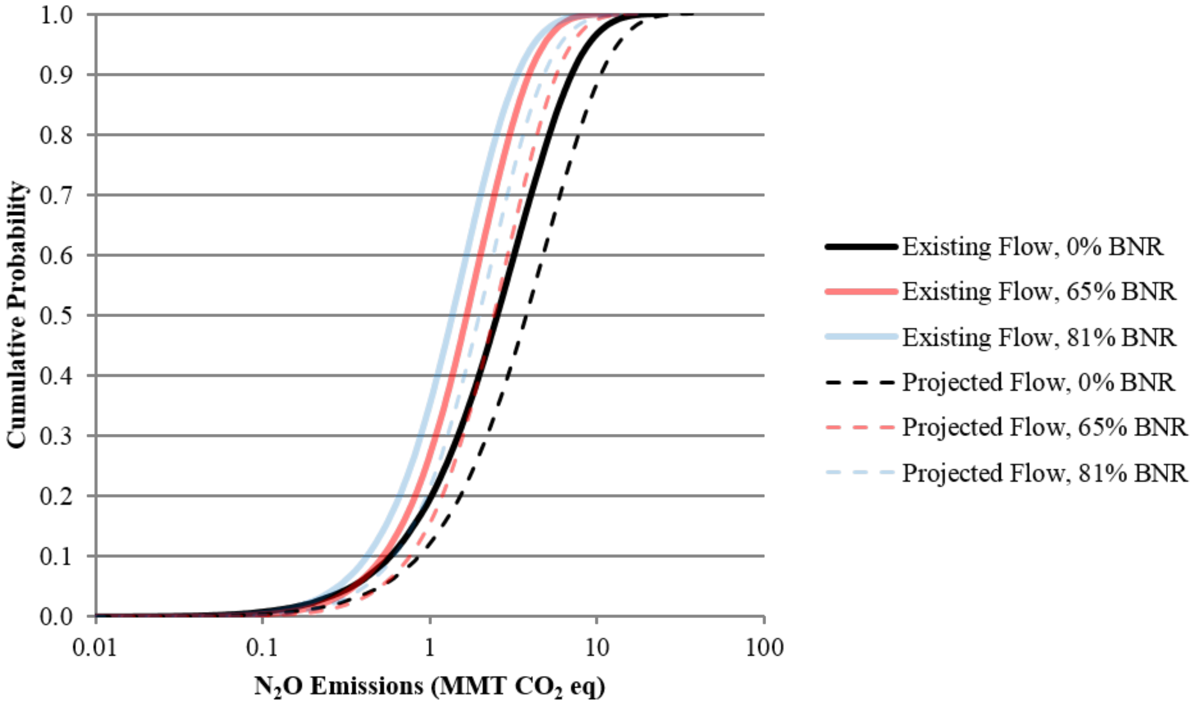

Figure C.1. Total N2O emissions in the Chesapeake Bay Watershed

C.3 In-plant N_2O Emission Factors

Table C.2. Data points used for distribution fitting

Source	% Influent TKN emitted as N_2O	BNR?
Sumer et al. (1995)	0.001	No
Ahn et al. (2010)	0.01	Yes
Sommer et al. (1998)	0.02	No
Ahn et al. (2010)	0.03	No
Ahn et al. (2010)	0.03	Yes
Czepiel et al. (1995)	0.035	No
Aboobaker et al. (2013)	0.036	No
Ahn et al. (2010)	0.05	Yes
Ahn et al. (2010)	0.06	Yes
Ahn et al. (2010)	0.07	Yes
Ahn et al. (2010)	0.09	No
Ahn et al. (2010)	0.16	Yes
Ahn et al. (2010)	0.18	No
Ahn et al. (2010)	0.24	No
Foley et al. (2010)	0.28	Yes
Foley et al. (2010)	0.38	Yes
Ahn et al. (2010)	0.4	No
Ahn et al. (2010)	0.41	No
Foley et al. (2010)	0.42	Yes
Foley et al. (2010)	0.42	Yes
Foley et al. (2010)	0.45	Yes
Foley et al. (2010)	0.47	Yes
Ahn et al. (2010)	0.54	No
Foley et al. (2010)	0.56	Yes
Foley et al. (2010)	0.58	Yes
Ahn et al. (2010)	0.6	Yes
Ahn et al. (2010)	0.62	No
Ahn et al. (2010)	0.62	Yes
Foley et al. (2010)	0.72	Yes
Foley et al. (2010)	0.81	Yes
Foley et al. (2010)	0.91	Yes
Foley et al. (2010)	0.92	Yes
Foley et al. (2010)	0.99	Yes
Foley et al. (2010)	1.19	Yes

Foley et al. (2010)	1.19	Yes
Weissenbacher et al. (2010)	1.3	Yes
Foley et al. (2010)	1.38	Yes
Ahn et al. (2010)	1.5	Yes
Ahn et al. (2010)	1.6	Yes
Ahn et al. (2010)	1.8	No
Kampschreur et al. (2008)	2.3	Yes
Daelman et al. (2013)	2.8	Yes
Kampschreur et al. (2008)	4	No
Foley et al. (2010)	4.13	Yes
Foley et al. (2010)	4.20	Yes
Desloover et al. (2011)	5.1	Yes
Foley et al. (2010)	5.17	Yes
Foley et al. (2010)	11.84	Yes

Note: Emission factors taken from Foley et al. (2010) were calculated after retrieving additional nitrogen flow data through personal communications with Dr. Paul Lant

C.4 Converting from g N_2O/PE-yr to % of influent nitrogen emitted as N_2O

The conversion used in Kampschreur et al. (2009) was adopted here. This includes an assumption of 100 grams of protein consumed per person per day and also that protein consists of 16% nitrogen by weight.

$$EF\ (\%\ N\ emitted\ as\ N_2O) = \frac{\left(EF\left(\frac{g\ N_2O}{PE * yr}\right) * \frac{28}{44}\frac{g\ N}{g\ N_2O}\right)}{100\frac{g\ protein}{person * day} * 365\frac{days}{yr} * 0.16\frac{g\ N}{g\ protein}} * 100$$

References

[1] Aboobakar, A., Cartmell, E., Stephenson, T., Jones, M., Vale, P., and Dotro, G. (2013). "Nitrous oxide emissions and dissolved oxygen profiling in a full-scale nitrifying activated sludge treatment plant." *Water Research*, 47(2), 524-534.

[2] Ahn, J. H., Kim, S., Park, H., Rahm, B., Pagilla, K., and Chandran, K. (2010). "N2O Emissions from Activated Sludge Processes, 2008–2009: Results of a National Monitoring Survey in the United States." *Environmental Science & Technology*, 44(12), 4505-4511.

[3] Amy, G., Siddiqui, M. S., Zhai, W., DeBroux, J., and Odem, W. "Nation-wide survey of bromide ion concentrations in drinking water sources." *Proc., American Water Works Association Annual Conference*, 1-19.

[4] Amy, G., Siddiqui, M. S., Zhai, W., DeBroux, J., and Odem, W. (1994). "Survey of Bromide in Drinking Water and Impacts on DBP Formation." American Water Works Research Foundation, Denver, CO.

[5] Anderson, D. M., Glibert, P. M., and Burkholder, J. M. (2002). "Harmful algal blooms and eutrophication: Nutrient sources, composition, and consequences." *Estuaries*, 25(4), 704-726.

[6] Barton, P., and Atwater, J. (2002). "Nitrous Oxide Emissions and the Anthropogenic Nitrogen in Wastewater and Solid Waste." *Journal of Environmental Engineering*, 128(2), 137-150.

[7] Beaulieu, J. J., Shuster, W. D., and Rebholz, J. A. (2010). "Nitrous Oxide Emissions from a Large, Impounded River: The Ohio River." *Environmental Science & Technology*, 44(19), 7527-7533.

[8] Beaulieu, J. J., Tank, J. L., Hamilton, S. K., Wollheim, W. M., Hall, R. O., Mulholland, P. J., Peterson, B. J., Ashkenas, L. R., Cooper, L. W., Dahm, C. N., Dodds, W. K., Grimm, N. B., Johnson, S. L., McDowell, W. H., Poole, G. C., Valett, H. M., Arango, C. P., Bernot, M. J., Burgin, A. J., Crenshaw, C. L., Helton, A. M., Johnson, L. T., O'Brien, J. M., Potter, J. D., Sheibley, R. W., Sobota, D. J., and Thomas, S. M. (2011). "Nitrous oxide emission from denitrification in stream and river networks." *PNAS*, 108(1), 214-219.

[9] Boesch, D. F., Brinsfield, R. B., and Magnien, R. E. (2001). "Chesapeake Bay Eutrophication." *Journal of Environment Quality*, 30(2), 303.

[10] Bowen, J. L., and Valiela, I. (2001). "The ecological effects of urbanization of coastal watersheds: historical increases in nitrogen loads and eutrophication of Waquoit Bay estuaries." *Can. J. Fish. Aquat. Sci.*, 58(8), 1489-1500.

[11] California Division of Drinking Water (2015). "Drinking Water Notification Levels and Response Levels: An Overview." <https://www.waterboards.ca.gov/drinking_water/certlic/drinkingwater/documents/notificationlevels/notificationlevels.pdf>.

[12] Cantor, K., Lynch, C., Hildesheim, M., Dosemeci, M., Lubin, J., Alavanja, M., and Craun, G. (1998). "Drinking water source and chlorination byproducts I. Risk of bladder cancer." *Epidemiology*, 9(1), 21-28.

[13] Cantor, K. P., Villanueva, C. M., Silverman, D. T., Figueroa, J. D., Real, F. X., Garcia-Closas, M., Malats, N., Chanock, S., Yeager, M., and Tardon, A. (2010).

"Polymorphisms in GSTT1, GSTZ1, and CYP2E1, disinfection by-products, and risk of bladder cancer in Spain." *Environmental health perspectives*, 118(11).

[14] Cedergren, M. I., Selbing, A. J., Löfman, O., and Källen, B. A. J. (2002). "Chlorination Byproducts and Nitrate in Drinking Water and Risk for Congenital Cardiac Defects." *Environmental Research*, 89(2), 124-130.

[15] Chen, B., Nam, S. N., Westerhoff, P. K., Krasner, S. W., and Amy, G. (2009). "Fate of effluent organic matter and DBP precursors in an effluent-dominated river: a case study of wastewater impact on downstream water quality." *Water Research*, 43, 1755-1765.

[16] Chisholm, K., Cook, A., Bower, C., and Weinstein, P. (2008). "Risk of birth defects in Australian communities with high levels of brominated disinfection by-products." *Environmental Health Perspectives*, 116(9), 1267-1273.

[17] Chuang, Y.-H., and Mitch, W. A. (2017). "Effect of Ozonation and Biological Activated Carbon Treatment of Wastewater Effluents on Formation of N-nitrosamines and Halogenated Disinfection Byproducts." *Environmental Science & Technology*, 51(4), 2329-2338.

[18] Clough, T. J., Bertram, J. E., Sherlock, R. R., Leonard, R. L., and Nowicki, B. L. (2006). "Comparison of measured and EF5-r-derived N2O fluxes from a spring-fed river." *Global Change Biology*, 12(3), 477-488.

[19] Cole, J. J., and Caraco, N. F. (2001). "Emissions of Nitrous Oxide (N2O) from a Tidal, Freshwater River, the Hudson River, New York." *Environmental Science & Technology*, 35(6), 991-996.

[20] Czepiel, P., Crill, P., and Harriss, R. (1995). "Nitrous Oxide Emissions from Municipal Wastewater Treatment." *Environmental Science & Technology*, 29(9), 2352-2356.

[21] Daelman, M. R. J., van Voorthuizen, E. M., van Dongen, L. G. J. M., Volcke, E. I. P., and van Loosdrecht, M. C. M. (2013). "Methane and nitrous oxide emissions from municipal wastewater treatment - results from a long-term study." *Water Sci. Technol.*, 67(10), 2350-2355.

[22] Dai, N., Zeng, T., and Mitch, W. A. (2015). "Predicting N-Nitrosamines: N-Nitrosodiethanolamine as a Significant Component of Total N-Nitrosamines in Recycled Wastewater." *Environmental Science & Technology Letters*, 2(3), 54-58.

[23] Desloover, J., De Clippeleir, H., Boeckx, P., Du Laing, G., Colsen, J., Verstraete, W., and Vlaeminck, S. E. (2011). "Floc-based sequential partial nitritation and anammox at full scale with contrasting N2O emissions." *Water Research*, 45(9), 2811-2821.

[24] Dong, L. F., Nedwell, D. B., Colbeck, I., and Finch, J. (2005). "Nitrous oxide emission from some English and Welsh rivers and estuaries." *Water Air Soil Pollut: Focus*, 4(6), 127-134.

[25] Doorn, M. R. J., Strait, R., Barnard, W., and Eklund, B. (1997). "Estimate of Global Greenhouse Gas Emissions from Industrial and Domestic Wastewater Treatment." ARCADIS, Research Triangle Park, NC.

[26] Echigo, S., Itoh, S., Natsui, T., Araki, T., and Ando, R. (2004). "Contribution of brominated organic disinfection by-products to the mutagenicity of drinking water." *Water Science and Technology*, 50(5), 321-328.

[27] Flury, M., and Papritz, A. (1993). "Bromide in the natural environment: occurrence and toxicity." *Journal of Environmental Quality*, 22(4), 747-758.

[28] Foley, J., de Haas, D., Yuan, Z., and Lant, P. (2010). "Nitrous oxide generation in full-scale biological nutrient removal wastewater treatment plants." *Water Research*, 44(3), 831-844.

[29] Foley, J., Yuan, Z., Keller, J., Senante, E., Chandran, K., Willis, J., Shah, A., van Loosdrecht, M., and van Voorthuizen, E. (2011). *N2O and CH4 emission from wastewater collection and treatment systems: technical report*, Global Water Research Coalition.

[30] Francis, R., VanBriesen, J., and Small, M. (2010a). "Bayesian Statistical Modeling of Disinfection Byproduct (DBP) Bromine Incorporation in the ICR Database." *Environmental Science and Technology*, 44(4), 1232-1239.

[31] Francis, R. A., VanBriesen, J. M., and Small, M. J. (2010b). "Bayesian Statistical Modeling of Disinfection Byproduct (DBP) Bromine Incorporation in the ICR Database." *Environmental Science and Technology*, 44(4), 1232-1239.

[32] Ged, E. C., and Boyer, T. H. (2014). "Effect of seawater intrusion on formation of bromine-containing trihalomethanes and haloacetic acids during chlorination." *Desalination*, 345, 85-93.

[33] Gerrity, D., Pisarenko, A. N., Marti, E., Trenholm, R. A., Gerringer, F., Reungoat, J., and Dickenson, E. (2015). "Nitrosamines in pilot-scale and full-scale wastewater treatment plants with ozonation." *Water Research*, 72, 251-261.

[34] Good, K. D., and VanBriesen, J. M. (2016). "Current and potential future bromide loads from coal-fired power plants in the Allegheny River Basin and their effects on downstream concentrations." *Environmental Science and Technology*, 50(17), 9078-9088.

[35] Greening, H., and Janicki, A. (2006). "Toward Reversal of Eutrophic Conditions in a Subtropical Estuary: Water Quality and Seagrass Response to Nitrogen Loading Reductions in Tampa Bay, Florida, USA." *Environmental Management*, 38(2), 163-178.

[36] Greune, A. (2014). "Bromide Occurrence in North Carolina and the Relationship between Bromide Concentration and Trihalomethane Formation." M.S., North Carolina State University.

[37] Hagy, J. D., Boynton, W. R., Keefe, C. W., and Wood, K. V. (2004). "Hypoxia in Chesapeake Bay, 1950–2001: Long-term change in relation to nutrient loading and river flow." *Estuaries*, 27(4), 634-658.

[38] Hanigan, D., Zhang, J., Herckes, P., Krasner, S. W., Chen, C., and Westerhoff, P. (2012). "Adsorption of N-Nitrosodimethylamine Precursors by Powdered and Granular Activated Carbon." *Environmental Science & Technology*, 46(22), 12630-12639.

[39] Hess, D. E. (2016). "Water Released From NY Reservoir For First Time To Deal With Susquehanna Drought." *PA Environment Digest*, Crisci Associates.

[40] Hong, H., Liang, Y., Han, B., Mazumder, A., and Wong, M. (2007). "Modeling of trihalomethane (THM) formation via chlorination of the water from Dongjiang River (source water for Hong Kong's drinking water)." *Science of the Total Environment*, 385, 48-54.

[41] Hrudey, S. E., and Charrois, J. W. (2012). "Disinfection by-products and human health." IWA Publishing, London, UK.

[42] Hua, G., and Reckhow, D. A. (2012). "Evaluation of bromine substitution factors of DBPs during chlorination and chloramination." *Water Research*, 46, 4208-4216.

[43] Hua, G., Reckhow, D. A., and Kim, J. (2006). "Effect of bromide and iodide ions on the formation and speciation of disinfection byproducts during chlorination." *Environmental Science and Technology*, 40, 3050-3056.

[44] IPCC (2006). "2006 IPCC Guidelines for National Greenhouse Gas Inventories." H. S. Eggleston, L. Buendia, K. Miwa, T. Ngara, and K. Tanabe, eds., National Greenhouse Gas Inventories Programme, IGES, Japan.

[45] Kampschreur, M. J., Temmink, H., Kleerebezem, R., Jetten, M. S. M., and van Loosdrecht, M. C. M. (2009). "Nitrous oxide emission during wastewater treatment." *Water Research*, 43(17), 4093-4103.

[46] Kampschreur, M. J., van der Star, W. R. L., Wielders, H. A., Mulder, J. W., Jetten, M. S. M., and van Loosdrecht, M. C. M. (2008). "Dynamics of nitric oxide and nitrous oxide emission during full-scale reject water treatment." *Water Research*, 42(3), 812-826.

[47] Kemp, W. M., Boynton, W. R., Adolf, J. E., Boesch, D. F., Boicourt, W. C., Brush, G., Cornwell, J. C., Fisher, T. R., Glibert, P. M., Hagy, J. D., Harding, L. W., Houde, E. D., Kimmel, D. G., Miller, W. D., Newell, R. I. E., Roman, M. R., Smith, E. M., and Stevenson, J. C. (2005). "Eutrophication of Chesapeake Bay: historical trends and ecological interactions." *Mar Ecol Prog Ser*, 303, 1-29.

[48] Kolb, C., Francis, R., and VanBriesen, J. (2017). "Disinfection by-product regulatory compliance surrogates and bromide-associated risk." *Journal of Environmental Sciences*, in press

[49] Krasner, S., Westerhoff, P., Chen, B., Amy, G., Nam, S., Chowdhury, Z., Sinha, S., and Rittmann, B. (2008). *Contribution of wastewater to DBP formation*, Water Environment Research Foundation.

[50] Krasner, S., Westerhoff, P., Chen, B., Rittmann, B., Nam, S.-N., and Amy, G. (2009a). "Impact of wastewater treatment processes on organic carbon, organic nitrogen, and DBP precursors in effluent organic matter." *Environmental Science and Technology*, 43(8), 2911-2918.

[51] Krasner, S. W., Mitch, W. A., McCurry, D. L., Hanigan, D., and Westerhoff, P. (2013). "Formation, precursors, control, and occurrence of nitrosamines in drinking water: A review." *Water Research*, 47(13), 4433-4450.

[52] Krasner, S. W., Sclimenti, M. J., and Means, E. J. (1994). "Quality degradation: implications for DBP formation." *Journal of American Water Works Association*, 96(6), 34-47.

[53] Krasner, S. W., Westerhoff, P., Chen, B., Rittmann, B. E., and Amy, G. (2009b). "Occurrence of Disinfection Byproducts in United States Wastewater Treatment Plant Effluents." *Environmental Science & Technology*, 43(21), 8320-8325.

[54] Kristiana, I., Liew, D., Henderson, R. K., Joll, C. A., and Linge, K. L. (2017). "Formation and control of nitrogenous DBPs from Western Australian source waters: Investigating the impacts of high nitrogen and bromide concentrations." *Journal of Environmental Sciences*, 58(Supplement C), 102-115.

[55] Lee, C.-F. T., Krasner, S. W., Sclimenti, M. J., Prescott, M., and Guo, Y. C. (2015). "Nitrosamine Precursors and Wastewater Indicators in Discharges in the Sacramento-San Joaquin Delta." *Recent Advances in Disinfection By-Products*, American Chemical Society, 119-133.

[56] Li, Z., Clark, R. M., Buchberger, S. G., and Yang, Y. J. (2014). "Evaluation of climate change impact on drinking water treatment plant operation." *Journal of Environmental Engineering*, 140, A4014005.

[57] Liu, X.-L., Bai, L., Wang, Z.-L., Li, J., Yue, F.-J., and Li, S.-L. (2015). "Nitrous oxide emissions from river network with variable nitrogen loading in Tianjin, China." *Journal of Geochemical Exploration*, 157, 153-161.

[58] Luong, T., Peters, C., Young, R., and Perry, R. (1980). "Bromide and trihalomethanes in water supplies." *Environmental Technology Letters*, 1(6), 299-310.

[59] Magnus, P., Jaakkola, J. J. K., Skrondal, A., Alexander, J., Becker, G., Krogh, T., and Dybing, E. (1999). "Water Chlorination and Birth Defects." *Epidemiology*, 10(5), 513-517.

[60] Mann, H. B., and Whitney, D., R. (1947). "On a Test of Whether one of Two Random Variables is Stochastically Larger than the Other." *The Annals of Mathematical Statistics*, 18(1), 50-60.

[61] Mao, Y., Wang, X., Yang, H., Wang, H., and Xie, Y. F. (2014). "Effects of ozonation on disinfection byproduct formation and speciation during subsequent chlorination." *Chemosphere*, 117, 515-520.

[62] McGuire, M. J., McLain, J. L., and Obolensky, A. (2002). "Information Collection Rule Data Analysis." American Water Works Association Research Foundation, Denver CO.

[63] Mitch, W., Sharp, J. O., Trussell, R. R., Valentine, R. L., Alvarez-Cohen, L., and Sedlak, D. L. (2004). "N-Nitrosodimethylamine (NDMA) as a Drinking Water Contaminant: A Review." *Environmental Engineering Science*.

[64] Mitch, W. A., and Sedlak, D. L. (2004). "Characterization and Fate of N-Nitrosodimethylamine Precursors in Municipal Wastewater Treatment Plants." *Environmental Science & Technology*, 38(5), 1445-1454.

[65] Mosier, A., Kroeze, C., Nevison, C., Oenema, O., Seitzinger, S., and Cleemput, O. v. (1998). "Closing the global N2O budget: nitrous oxide emissions through the agricultural nitrogen cycle." *Nutrient Cycling in Agroecosystems*, 52(2-3), 225-248.

[66] Muellner, M. G., Wagner, E. D., McCalla, K., Richardson, S. D., Woo, Y.-T., and Plewa, M. J. (2007). "Haloacetonitriles vs. Regulated Haloacetic Acids:□ Are Nitrogen-Containing DBPs More Toxic?" *Environmental Science & Technology*, 41(2), 645-651.

[67] Munch, J., and Bassett, M. (2004). "Method 521 determination of nitrosamines in drinking water by solid phase extraction and capillary column gas chromatography with large volume injection and chemical ionization tandem mass spectrometry (MS/MS)." *National Exposure Research Laboratory Office of Research and Development, US Environmental Protection Agency, Cincinnati*.

[68] National Water Quality Monitoring Council (2017). "Water Quality Data." <https://www.waterqualitydata.us/portal/ >. (April 25, 2017).

[69] NEBRA (2007). "A National Biosolids Regulation, Quality, End Use & Disposal Survey." North East Biosolids and Residuals Association, Tamworth, NH.

[70] Ni, B.-J., Yuan, Z., Chandran, K., Vanrolleghem, P. A., and Murthy, S. (2013). "Evaluating four mathematical models for nitrous oxide production by autotrophic ammonia-oxidizing bacteria." *Biotechnol. Bioeng.*, 110(1), 153-163.

[71] NTP (1987). "NTP Toxicology and Carcinogenesis Studies of Bromodichloromethane (CAS No. 75-27-4) in F344/N Rats and B6C3F1 Mice (Gavage Studies)." *National Toxicology Program technical report series*, 321, 1-182.

[72] NTP (1985). "NTP Toxicology and Carcinogenesis Studies of Chlorodibromomethane (CAS No. 124-48-1) in F344/N Rats and B6C3F1 Mice (Gavage Studies)." *National Toxicology Program technical report series*, 282, 1-174.

[73] NTP (1989). "NTP Toxicology and Carcinogenesis Studies of Tribromomethane (Bromoform) (CAS No. 75-25-2) in F344/N Rats and B6C3F1 Mice (Gavage Studies)." *National Toxicology Program technical report series*, 350, 1-194.

[74] Obolensky, A., and Singer, P. C. (2005). "Halogen substitution patterns among disinfection byproducts in the Information Collection Rule database." *Environmental Science and Technology*, 39, 2719-2730.

[75] Obolensky, A., Singer, P. C., and Shukairy, H. M. (2007). "Information collection rule data evaluation and analysis to support impacts on disinfection by-product formation." *J. Environ. Eng.-ASCE*, 133(1), 53-63.

[76] PADEP (2017a). "Drinking Water Electronic Lab Reporting System." <http://www.dep.pa.gov/Citizens/My-Water/PublicDrinkingWater/Pages/Electronic-Reporting-System.aspx>. (March 23, 2017).

[77] PADEP (2016). "Drinking Water Reporting System." <http://www.drinkingwater.state.pa.us/dwrs/HTM/Welcome.html>. (January 12, 2017).

[78] PADEP (2017b). "Water Quality Network." <http://www.dep.pa.gov/Business/Water/CleanWater/WaterQuality/Pages/Water-Quality-Network.aspx>. (April 29, 2017, 2017).

[79] Pearson, K. (1895). "Note on regression and inheritance in the case of two parents." *Proceedings of the Royal Society of London*, 58, 240-242.

[80] Pearson, K. (1900). "X. On the criterion that a given system of deviations from the probable in the case of a correlated system of variables is such that it can be reasonably supposed to have arisen from random sampling." *The London, Edinburgh, and Dublin Philosophical Magazine and Journal of Science*, 50(302), 157-175.

[81] Peto, R., Gray, R., Brantom, P., and Grasso, P. (1984). "Nitrosamine carcinogenesis in 5120 rodents: chronic administration of sixteen different concentrations of NDEA, NDMA, NPYR and NPIP in the water of 4440 inbred rats, with parallel studies on NDEA alone of the effect of age of starting (3, 6 or 20 weeks) and of species (rats, mice or hamsters)." *IARC scientific publications*(57), 627-665.

[82] Plewa, M. J., Kargalioglu, Y., Vankerk, D., Minear, R. A., and Wagner, E. D. (2002). "Mammalian cell cytotoxicity and genotoxicity analysis of drinking water disinfection by-products." *Environmental and Molecular Mutagenesis*, 40(2), 134-142.

[83] Plewa, M. J., Wagner, E. D., Muellner, M. G., Hsu, K.-M., and Richardson, S. D. (2008). "Comparative Mammalian Cell Toxicity of N-DBPs and C-DBPs." *Disinfection By-Products in Drinking Water*, American Chemical Society, 36-50.

[84] Plewa, M. J., Wagner, E. D., Richardson, S. D., Thruston, A. D., Woo, Y. T., and McKague, A. B. (2004). "Chemical and biological characterization of newly discovered iodoacid drinking water disinfection byproducts." *Environmental Science and Technology*, 38(18), 4713-4722.

[85] Rathbun, R. E. (1996). "Speciation of trihalomethane mixtures for the Mississippi, Missouri, and Ohio Rivers." *Science of the Total Environment*, 180(2), 125-135.

[86] Ravishankara, A. R., Daniel, J. S., and Portmann, R. W. (2009). "Nitrous Oxide (N2O): The Dominant Ozone-Depleting Substance Emitted in the 21st Century." *Science*, 326(5949), 123-125.

[87] Regli, S., Chen, J., Messner, M., Elovitz, M., Letkiewicz, F., Pegram, R., Pepping, T., Richardson, S., and Wright, J. (2015). "Estimating potential increased bladdar cancer risk due to increased bromide concentrations in sources of disinfected drinking waters." *Environmental Science and Technology*, 49(22), 13094-13102.

[88] Rice, J., Via, S. H., and Westerhoff, P. (2015). "Extent and Impacts of Unplanned Wastewater Reuse in US Rivers." *Journal - American Water Works Association*, 107, E571-E581.

[89] Rice, J., and Westerhoff, P. (2015). "Spatial and Temporal Variation in De Facto Wastewater Reuse in Drinking Water Systems across the U.S.A." *Environmental Science & Technology*, 49(2), 982-989.

[90] Rice, J., Wutich, A., and Westerhoff, P. (2013). "Assessment of De Facto Wastewater Reuse across the U.S.: Trends between 1980 and 2008." *Environmental Science & Technology*, 47(19), 11099-11105.

[91] Richardson, S. D., Plewa, M. J., Wagner, E. D., Schoeny, R., and DeMarini, D. M. (2007). "Occurrence, genotoxicity, and carcinogenicity of regulated and emerging disinfection by-products in drinking water: A review and roadmap for research." *Mutation Research/Reviews in Mutation Research*, 636(1–3), 178-242.

[92] Roberson, J. (2002). "An Inventory of ICR Systems, Treatment Plants, and Source Water Supplies." *Information Collection Rule Data Analysis*, M. McGuire, J. McLain, and A. Obolensky, eds., American Water Works Association Research Foundation, Denver, CO, 67-80.

[93] Roccaro, P., Vagliasindi, F. G., and Korshin, G. V. (2011). "Quantifying the formation of nitrogen-containing disinfection by-products in chlorinated water using absorbance and fluorescence indexes." *Water science and technology : a journal of the International Association on Water Pollution Research*, 63(1), 40-44.

[94] Rodriguez-Caballero, A., Aymerich, I., Poch, M., and Pijuan, M. (2014). "Evaluation of process conditions triggering emissions of green-house gases from a biological wastewater treatment system." *Science of The Total Environment*, 493, 384-391.

[95] Russell, C. G., Blute, N. K., Via, S., Wu, X., and Chowdhury, Z. (2012). "Nationwide assessment of nitrosamine occurrence and trends." *Journal - American Water Works Association*, 104.

[96] Salas, L. A., Cantor, K. P., Tardon, A., Serra, C., Carrato, A., Garcia-Closas, R., Rothman, N., Malats, N., Silverman, D., Kogevinas, M., and Villanueva, C. M. (2013). "Biological and Statistical Approaches for Modeling Exposure to Specific Trihalomethanes and Bladder Cancer Risk." *American Journal of Epidemiology*, 178(4), 652-660.

[97] Scheehle, E. A., and Doorn, M. R. J. (2001). "Improvements to the U.S. Wastewater Methane and Nitrous Oxide Emissions Estimates."

[98] Schön, M., Walz, R., Angerer, G., Bätcher, K., and Böhm, E. (1993). "Emissionen der Treibhausgase Distickstoffoxid und Methan in Deutschland." *Umweltbundesamt. National Environmental Agency, Berlin*, 189.

[99] Schreiber, F., Wunderlin, P., Udert, K. M., and Wells, G. F. (2012). "Nitric oxide and nitrous oxide turnover in natural and engineered microbial communities: biological pathways, chemical reactions, and novel technologies." *Front Microbiol*, 3.

[100] Schreiber, I. M., and Mitch, W. A. (2006). "Occurrence and Fate of Nitrosamines and Nitrosamine Precursors in Wastewater-Impacted Surface Waters Using Boron As a Conservative Tracer." *Environmental Science & Technology*, 40(10), 3203-3210.

[101] Seitzinger, S. P., and Kroeze, C. (1998). "Global distribution of nitrous oxide production and N inputs in freshwater and coastal marine ecosystems." *Global Biogeochemical Cycles*, 12(1), 93-113.

[102] Sgroi, M., Vagliasindi, F. G. A., Snyder, S. A., and Roccaro, P. (2018). "N-Nitrosodimethylamine (NDMA) and its precursors in water and wastewater: A review on formation and removal." *Chemosphere*, 191(Supplement C), 685-703.

[103] Singer, P. C. (1994). "Control of Disinfection By-Products in Drinking Water." *Journal of Environmental Engineering*, 120(4), 727-744.

[104] Singer, P. C. (2004). "Disinfection by-products in US drinking waters: past, present and future." *Water Science and Technology: Water Supply*, 4(1), 151-157.

[105] Smirnov, N. (1948). "Table for Estimating the Goodness of Fit of Empirical Distributions." *The Annals of Mathematical Statistics*, 19(2), 279-281.

[106] Sohn, J., Amy, G., and Yoon, Y. (2006). "Bromide ion incorporation into brominated disinfection by-products." *Water, Air and Soil Pollution*, 174(1), 265-277.

[107] Sommer, J., Ciplak, G., Linn, A., Sumer, E., Benckiser, G., and Ottow, J. C. G. (1998). "Quantification of emitted and retained N2O in a municipal waste water treatment plant with activated sludge and nitrifying-denitrifying units." *Agribiological research*, 51(1), 59-73.

[108] States, S., Cyprych, G., Stoner, M., Wydra, F., Kuchta, J., Monnell, J., and Casson, L. (2013). "Marcellus shale drilling and brominated THMs in Pittsburgh, PA, drinking water." *Journal of the American Water Works Association*, 105(8), E432-E448.

[109] Sümer, E., Weiske, A., Benckiser, G., and Ottow, J. C. G. (1995). "Influence of environmental conditions on the amount of N2O released from activated sludge in a domestic waste water treatment plant." *Experientia*, 51(4), 419-422.

[110] Swayne, M., Boone, G., Bauer, D., and Lee, J. (1980). "Wastewater in Receiving Waters at Water Supply Abstraction Points." U.S. Environmental Protection Agency, Washington, D.C.

[111] Tchobanoglous, G., and Burton, F. L. (1991). *Wastewater Engineering: Treatment, Disposal, and Reuse*, McGraw-Hill, New York.

[112] Tian, C., Liu, R., Guo, T., Liu, H., Luo, Q., and Qu, J. (2013). "Chlorination and chloramination of high bromide natural water: DBPs species transformation " *Separation and Purification Technology*, 102, 86-93.

[113] Turner, P. A., Griffis, T. J., Lee, X., Baker, J. M., Venterea, R. T., and Wood, J. D. (2015). "Indirect nitrous oxide emissions from streams within the US Corn Belt scale with stream order." *PNAS*, 112(32), 9839-9843.

[114] US Census Bureau (2013). "U.S. Census Bureau International Database (IDB)." U.S. Census Bureau.

[115] US Department of Agriculture (2012). "Economic Rsearch Data sets, Data Sets, U.S. Fertilizer Imports/Exports: Standard Tables."

[116] US Geological Survey (2014). "National Watershed Boundary Dataset (WBD)."

[117] USEPA (1999). "Biosolids Generation, Use and Disposal in the United States." Office of Solid Waste, U.S.Environmental Protection Agency.

[118] USEPA (2017a). "Bromodichloromethane; CASRN 75-27-4."

[119] USEPA (2012a). "Clean Watersheds Needs Survey 2008 Report to Congress." Office of Wastewater Management, Washington, DC.

[120] USEPA (2016a). "Clean Watersheds Needs Survey 2012 Report and Data." Office of Wastewater Management, Washington, DC.

[121] USEPA (2017b). "Dibromochloromethane; CASRN 124-48-1."

[122] USEPA (2009). "Drinking Water Contaminant Candidate
List 3—Final ", U.S. Environmental Protection Agency, Washington, DC, 51850-51862.

[123] USEPA (2016b). "Drinking Water Contaminant Candidate
List 4—Final ", U.S. Environmental Protection Agency, Washington, DC, 81099-81114.

[124] USEPA (2005a). "Drinking Water Criteria Document for Brominated Trihalomethanes." United States Environmental Protection Agency, Washington DC.

[125] USEPA (2005b). "Economic analysis for the final stage 2 disinfectants and disinfectant byproducts rule." U.S. Environmental Protection Agency, Washington DC.

[126] USEPA (2000a). "ICR Auxiliary 1 Database Version 5.0 Query Tool Version 2.0." U.S. Environmental Protection Agency, Washington, DC.

[127] USEPA (2016c). "Integrated Risk Information System."Arlington, VI.

[128] USEPA (2014). "Inventory of U.S. Greenhouse Gas Emissions and Sinks: 1990–2012."

[129] USEPA (1987). "N-Nitrosodimethylamine CASRN 62-75-9."

[130] USEPA (2006). "National primary drinking water regulations: Stage 2 disinfectant and disinfection byproduct rule." U.S. Environmental Protection Agency, Washington, DC, 388-493.

[131] USEPA (2012b). "Organic chemicals, sampling and analytical requirements." *40 CFR Part 141.24*, Federal Register, Washington, DC.

[132] USEPA (2000b). "The Risk Assessment of Mixtures of Disinfection By-Products (DBPs) in Drinking Water." United States Environmental Protection Agency, Cincinnati, OH.

[133] USEPA (2007). "Unregulated Contaminant Monitoring Regulation (UCMR) for Public Water Systems Revisions; Final Rule." U.S. Environmental Protection Agency, Washington, DC, 368-398.

[134] USGS (2017). "National Water Information System." <https://waterdata.usgs.gov/nwis/rt>. (April 12, 2017).

[135] Villanueva, C., Cantor, K., Grimalt, J., Malats, N., Silverman, D., Tardon, A., Garcia-Closas, R., Serra, C., Carrato, A., Castano-Vinyals, G., Marcos, R., Rothman, N., Real, F., Dosemeci, M., and Kogevinas, M. (2007a). "Bladder cancer and exposure to water disinfection by products through ingestion, bathing, showering and swimming in pools." *American Journal of Epidemiology*, 165(2), 148-156.

[136] Villanueva, C. M., Cantor, K. P., Cordier, S., Jaakkola, J. J. K., King, W. D., Lynch, C. F., Porru, S., and Kogevinas, M. (2004). "Disinfection Byproducts and Bladder Cancer: A Pooled Analysis." *Epidemiology*, 15(3), 357-367.

[137] Villanueva, C. M., Cantor, K. P., Grimalt, J. O., Malats, N., Silverman, D., Tardon, A., Garcia-Closas, R., Serra, C., Carrato, A., Castano-Vinyals, G., Marcos, R., Rothman, N., Real, F. X., Dosemeci, M., and Kogevinas, M. (2007b). "Bladder cancer and exposure to water disinfection by products through ingestion, bathing, showering and swimming in pools." *American Journal of Epidemiology*, 165(2), 148-156.

[138] Wang, G. S., Deng, Y. C., and Lin, T. F. (2007). "Cancer Risk Assessment from Trihalomethanes in drinking water." *Science for the Total Environment*, 387(1-3), 86-95.

[139] Wang, J. S., Hamburg, S. P., Pryor, D. E., Chandran, K., and Daigger, G. T. (2011). "Emissions Credits: Opportunity To Promote Integrated Nitrogen Management in the Wastewater Sector." *Environmental Science & Technology*, 45(15), 6239-6246.

[140] Wang, Y., Small, M. J., and VanBriesen, J. M. (2017). "Assessing the Risk Associated with Increasing Bromide in Drinking Water Sources in the Monongahela River, Pennsylvania." *Journal of Environmental Engineering*, 143(3), 04016089.

[141] Water Environment Federation (2011). *Nutrient removal*, McGraw-Hill ; WEF Press, New York : Alexandria, Va.

[142] Weaver, J., Xu, J., and Mravik, S. (2016). "Scenario Analysis of the Impact on Drinking Water Intakes from Bromide in the Discharge of Treated Oil and Gas Wastewater." *Journal of Environmental Engineering*, 142(1), 04015050.

[143] Weissenbacher, N., Takacs, I., Murthy, S., Fuerhacker, M., and Wett, B. (2010). "Gaseous Nitrogen and Carbon Emissions from a Full-Scale Deammonification Plant." *Water Environment Research*, 82(2), 169-175.

[144] Wilson, J. M., and VanBriesen, J. M. (2012). "Research Articles: Oil and Gas Produced Water Management and Surface Drinking Water Sources in Pennsylvania." *Environmental Practice*, 14(4), 288-300.

[145] Wilson, J. M., and VanBriesen, J. M. (2014). "Source water changes and energy extraction activities in the Monongahela River, 2009-2012." *Environmental Science and Technology*, 47(21), 12575-12582.

[146] Wilson, J. M., Wang, Y., and VanBriesen, J. M. (2013). "Sources of high total dissolved solids to drinking water supply in Southwestern Pennsylvania." *ASCE Journal of Environmental Engineering*, 140(Special Issue on Shale Gas Environmental Impacts), B4014003.

[147] World Health Organization (2017). *Guidelines for Drinking-water Quality: Fourth Edition Incorporating The First Addendum*, Geneva, Switzerland.

[148] Wysock, B. M., Cummins, M. D., Fair, P. S., Feirge, M. A., Sorrell, R. K., Walasek, J. B., and Bohl, B. J. (2002). "ICR Implementation and Data Collection Challenges." *Information Collection Rule Data Analysis*, M. J. McGuire, J. L. McLain, and A. Obolensky, eds., AWWA Research Foundation, 1-38.

[149] Yang, Y., Komaki, Y., Kimura, S. Y., Hu, H. Y., Wagner, E. D., Marinas, B., and Plewa, M. J. (2014). "Toxic impact of bromide and iodide on drinking water disinfected with chlorine and chloramines." *Environmental Science and Technology*, 48, 12362-12369.

[150] Yoshida, H., Clavreul, J., Scheutz, C., and Christensen, T. H. (2014). "Influence of data collection schemes on the Life Cycle Assessment of a municipal wastewater treatment plant." *Water Research*, 56, 292-303.

[151] Yu, Z., Deng, H., Wang, D., Ye, M., Tan, Y., Li, Y., Chen, Z., and Xu, S. (2013). "Nitrous oxide emissions in the Shanghai river network: implications for the effects of urban sewage and IPCC methodology." *Global Change Biology*, 19(10), 2999-3010.

[152] Zeng, T., Glover, C. M., Marti, E. J., Woods-Chabane, G. C., Karanfil, T., Mitch, W. A., and Dickenson, E. R. V. (2016). "Relative Importance of Different Water Categories as Sources of N-Nitrosamine Precursors." *Environmental Science & Technology*, 50(24), 13239-13248.

[153] Zhang, J., Yu, J., An, W., Liu, J., Wang, Y., Chen, Y., Tai, J., and Yang, M. (2011). "Characterization of disinfection byproduction formation potential in 13 source waters in China." *Journal of Environmental Sciences* 23(2), 183-188.