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N-Nitrosodimethylamine in Drinking Water: Temporal Formation Potential Patterns in Source Waters and Treatability of Precursors

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N-NITROSODIMETHYLAMINE IN DRINKING WATER: TEMPORAL FORMATION POTENTIAL PATTERNS IN SOURCE WATERS AND TREATABILITY OF PRECURSORS

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by
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ABSTRACT

The seasonal (summer, fall, winter and spring) and local weather related patterns of N-nitrosodimethylamine (NDMA) formation potentials (FPs) were examined with water samples collected monthly for a two year period in 12 surface waters. This long term study allowed monitoring the patterns of NDMA FPs under dynamic weather conditions (e.g., high/low rainfall periods) covering several seasons. Anthropogenically impacted source waters (SWs) which were determined by relatively high sucralose levels (>100 ng/L) had higher NDMA FPs than limited impacted SWs (<100 ng/L). In some sources, NDMA FP showed more variability in spring months. However, seasonal mean values were in general relatively consistent in most sources. These results showed that watershed characteristics played an important role in NDMA FP levels. For one of the sampled surface waters, a large reservoir on a river examined in this study appeared to serve as an equalization basin for NDMA precursors. In contrast, in a river without an upstream reservoir, the NDMA FP levels were influenced by the ratio of an upstream wastewater treatment plant (WWTP) effluent discharge to the river discharge rate. The impact of WWTP effluent decreased during the high river flow periods due to rain events. Linear regression with independent variables consisting of dissolved organic carbon (DOC), dissolved organic nitrogen (DON), and sucralose yielded poor correlations with NDMA FP ($R^2<0.27$). However, multiple linear regression analysis using DOC and log (sucralose) yielded a better correlation with NDMA FP ($R^2=0.53$).

This study also examined the removal of NDMA FPs for various operational conditions (e.g., alum clarification, powdered activated carbon [PAC] application, use of polymers, pre- and post-oxidation with chlorine [Cl_2] and/or chlorine dioxide [ClO_2], and Ct [concentration x contact time] changes) at full-scale water treatment plants (WTPs). The impacts of different seasons and dynamic local weather conditions (e.g., high/low rainfall periods) on the removal efficiency of NDMA FP at nine WTPs were investigated for a two year period. NDMA FP removal by alum clarification process remained between 12 to 30% for different seasons and temporal weather conditions. PAC addition (>4 mg/L) increased significantly the NDMA FP removal and PAC doses showed a good correlation (R^2=0.71) with the NDMA FP removal. The contribution of polymers to NDMA FP depended on the polymer type used and concentration. The simultaneous application of Cl_2 and ClO_2 for pre-oxidation and post-oxidation were beneficial for the removal of additional NDMA FPs. The average NDMA FP removals for reverse osmosis (RO) and microfiltration (MF) units were 81% and 7%, respectively.

The effect of ClO_2 oxidation on the control of NDMA precursors was investigated for different background waters (e.g., low/non-impacted vs. wastewater [WW]-impacted) under various oxidation conditions (e.g., pH, oxidant dose, and Ct). The removal of NDMA FP from all water types (low/non- or WW-impacted) was ≤25% at pH 6.0 with ClO_2 oxidation. However, under the similar oxidation conditions, NDMA FP removals increased up to ~80% with increasing influence (i.e., 10%, 25% and 50%) of WW effluents at pH 7.8. This indicates that the majority of WW-derived NDMA precursors can be deactivated with ClO_2 oxidation at higher pH (≥7.8). This was due to the better oxidative reaction of

ClO_2 with amines that have lone pair electrons to be shared at higher oxidation pH conditions. Similarly, NDMA formation levels under uniform formation condition (UFC) also significantly decreased in WW-impacted waters with ClO_2 oxidation at pH 7.8. Furthermore, natural attenuation simulation experiments were conducted in this study, and the results showed that ClO_2 oxidation can be more effective to deactivate NDMA precursors from relatively "freshly" impacted waters.

Finally, the effects of different oxidation scenarios (individual [ClO_2 or Cl_2 only] and integrated [simultaneous or sequential application of ClO_2 and Cl_2]) on the removal of NDMA FP from different waters (e.g., non-impacted vs. either 20% wastewater- or polymer-impacted waters) were investigated. The removal efficiency of NDMA FP in non-impacted waters for all the oxidation scenarios was ≤25%. In 20% WW-impacted waters, NDMA FP removals improved about 50% by only ClO_2 oxidation at pH 7.8 (~75%) compared to pH 6.0 (≤25%). However, the increase was limited for only Cl_2 oxidation case under same oxidation conditions. For integrated oxidations, NDMA FP removals increased (20-45%), especially, at pH 6.0 compared to individual application of oxidants (Cl_2 or ClO_2). This indicates that ClO_2 and Cl_2 can react with different amine precursors at lower pH (i.e., 6.0). However, increasing oxidation pH from 6.0 to 7.8 transformed amine precursors to more reactive forms for both oxidants. Furthermore, integrated use of Cl_2 and ClO_2 also increased (10-40%) the removal of polymer-derived (poly epichlorohydrin dimethylamine [polyamine], poly diallyldimethylammonium chloride [polyDADMAC] and polyacrylamide [Sedifloc 400C]) NDMA precursors independent of oxidation time (10 vs. 60 min) and pH (6.0 vs. 7.8).

DEDICATION

I would like to dedicate my work to my wife,

Seda Uzun

who has supported me throughout the process.

I also would like to dedicate this thesis to my parents,

Mehmet & **Gülşan Uzun**

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LIST OF ABBREVIATIONS

BET	Brunauer Emmett Teller
CA	California
C&D	Construction and Demolition
CDBP	Carbonaceous Disinfection By products
CCL	Contaminant Candidate List
CDPH	California Department of Public Health
Ct	Concentration x Contact Time
Da	Dalton
DAF	Dissolved Air Flotation
DBP	Disinfection By-product
DCM	Dichloromethane
D/DBPR	Disinfectants and Disinfection By Product Rule
DDW	Distilled and Deionized Water
DIN	Dissolved Inorganic Nitrogen
DL	Detection Limit
DMA	Dimethylamine
DN	Dissolved Nitrogen
DOC	Dissolved Organic Carbon
DON	Dissolved Organic Nitrogen
DPD	N,N-diethyl-p-phenylenediamine

EDA	Ethylenediamine
EEM-PARAFAC	Excitation-emission Matrices and Parallel Factor Analysis
EfOM	Effluent Organic Matter
EPA	Environmental Protection Agency
FP	Formation Potential
GC/ECD	Gas Chromatography/Electron Capture Detector
GLM	General Linear Model
HAA	Halo Acetic acid
HPLC	High Performance Liquid Chromatography
LASSO	Least absolute Shrinkage and Selection Operator
LRAA	Locational Running Annual Average
MCL	Maximum Contaminant Level
MF	Microfiltration
MG	Million Gallon
MGD	Million Gallon Per Day
MRDL	Maximum Residual Disinfectant Concentration
MRL	Minimum Reporting Limit
MS	Mass spectrometry
MtBE	Methyl Tertiary Butyl ether
MWCO	Molecular Weight Cutoff
N/A	Not applicable, Not Available or Not Measured
NDBA	N-nitrosodi-n-butylamine

N-DBP	Nitrogenous Disinfection By-product
NDEA	N-nitrosodiethylamine
NDMA	N-nitrosodimethylamine
NDMA-d_6	N-nitrosodimethylamine-d_6
NDPA	N-nitrosodi-n-propylamine
NDPA-d_{14}	N-nitrosodi-n-propylamine-d_{14}
NDPhA	N-nitrosodiphenyl-amine
NF	Nanofiltration
NMEA	N-nitroso-n-methylethylamine
NOB	North of Broad
NOM	Natural Organic Matter
NPDES	National Pollutant Discharge Elimination System
NPIP	N-nitrosopiperidine
NPYR	N-nitrosopyrrolidine
PAC	Powdered Activated Carbon
PDS	Precision Diluted Solutions
POE	Point of Entry
Polyamine	poly(epichlorohydrin dimethylamine)
PolyDADMAC	poly (diallyldimethylammonium chloride)
RO	Reverse Osmosis
SAS	Statistical Analysis System
SM	Standard Methods

SMP	Soluble Microbial Products
SOB	South of Broad
SUVA	Specific Ultraviolet Light Absorbance
SW	Source Water
THM	Trihalomethane
TOC	Total Organic Carbon
TOX	Total Organic Halide
UCMR 2	Unregulated Contaminant Monitoring Rule 2
UDMH	Unsymmetrical Dimethylhydrazine
UDMH-Cl	Chlorinated Unsymmetrical Dimethylhydrazine
UFC	Uniform Formation Condition
US	United States
USEPA	United States Environmental Protection Agency
USGS	United States Geological Survey
UV	Ultraviolet Light Absorbance
VOC	Volatile Organic Carbon
WTP	Water Treatment Plant
WW	Waste Water
WWTP	Waste Water Treatment Plant

CHAPTER ONE

INTRODUCTION

An increasing number of drinking water utilities in the United States (US) have been employing or considering chloramination for disinfection to comply with the stringent regulations for trihalomethanes (THMs) and haloacetic acids (HAAs). Texas, California, and Florida showed the most significant increases in switching to chloramination between 2007 and 2010 (Li, 2011). Nitrosamines constitute a class of disinfection by-products (DBPs) classified as probable human carcinogens in water at very low ng/L concentrations (USEPA, 2002); and they may occur primarily in chloraminated waters (Choi and Valentine, 2002a, 2002b; Mitch et al., 2003). As a result, there has been an increased attention on nitrosamines in the drinking water profession and by US Environmental Protection Agency (EPA).

Currently, (1) N-nitrosodimethylamine (NDMA), N-nitrosopyrrolidine (NPYR), N-nitrosodiethylamine (NDEA), N-nitrosodi-n-butylamine (NDBA), N-nitrosodi-n-propylamine (NDPA), and N-nitrosomethylethylamine (NMEA) have been included in Unregulated Contaminant Monitoring Rule 2 (UCMR2) (USEPA, 2012), and (2) NDMA, NDEA, NDPA, NPYR and N-nitrosodiphenyl-amine (NDPhA) have been included in the third version of the Contaminant Candidate List (CCL3) (USEPA, 2009). Chemical structures of nitrosamines (NDMA, NMEA, NDEA, NDPA, NDBA, N-nitrosopiperidine [NPIP] and NPYR) that can be detected by USEPA method 521 are shown in **Figure 1.1**. Among these nitrosamines, NDMA is the most commonly detected nitrosamine species in distribution systems that use chloramines for final disinfection in the US (Russell et al., 2012). Similarly, during EPA's UCMR2, NDMA was the most prevalent nitrosamine species: only less than 0.5% of samples collected nationwide were found to contain other nitrosamine species tested (USEPA, 2012; Woods and Dickenson, 2015). There is currently no federal regulations for nitrosamines in US drinking water systems. However, California Department of Public Health (CDPH) set 10 ng/L notification levels for three nitrosamine species (CDPH, 2004), and California’s Office of Environmental Health Hazard Assessment (OEHHA) also set a 3 ng/L public health goal for NDMA (OEHHA, 2006).

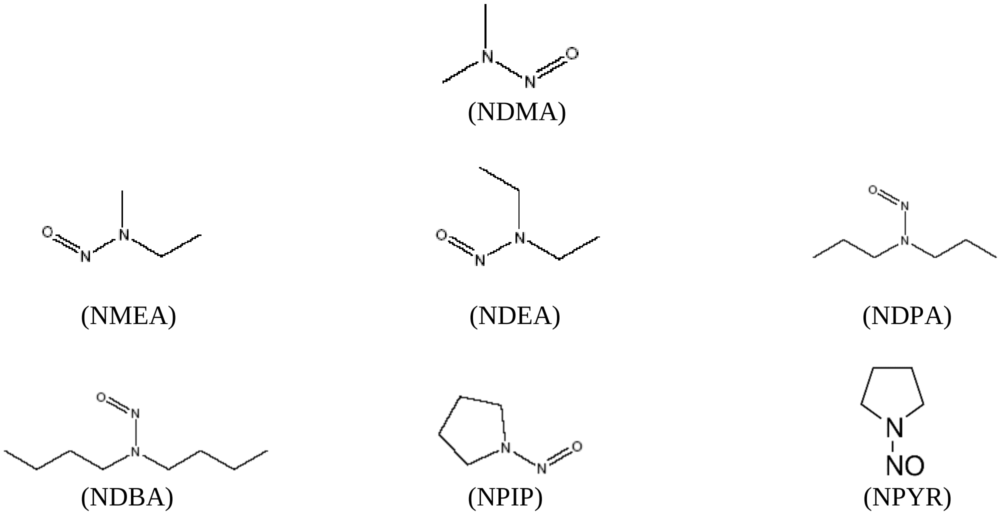

(NDMA)
(NMEA) (NDEA) (NDPA)
(NDBA) (NPIP) (NPYR)

Figure 1.1. Molecular structures of seven nitrosamine species that can be detected by USEPA method 521.

Therefore, considering possible future regulations, several US drinking water utilities have developed a strong interest in understanding the formation and control of NDMA in their systems. To better manage the water sources and treatment operations, the impacts of various temporal and climatic events (e.g., drought periods, spring run offs or major rains, algae growth/die off, seasonal effects, and lake turnovers) on the changes in the occurrences of NDMA precursors in source waters and its removal during water treatment need to be understood. A few studies have investigated seasonal effects on the NDMA precursors and evaluated possible relationships between NDMA precursors and water quality parameters (Aydin et al., 2012; Krasner et al., 2008; Mitch et al., 2009; Valentine et al., 2006; Zhang et al., 2014). However, conclusive results about the seasonal patterns of NDMA precursors from these studies have been lacking due to limited sample collection for limited time periods. Furthermore, the influence of watershed characteristics on the NDMA precursor levels in source waters has not been assessed. Although previous research has provided some information, comprehensive studies detailing the effect of dynamic events in watersheds on the occurrence and reactivity of NDMA and other nitrosamine precursors have been lacking in the literature.

One of the effective strategies to minimize NDMA formation in the distribution system would be to remove or deactivate NDMA precursors during water treatment before chloramination. Since the future NDMA regulations are expected to be at ng/L levels, many water treatment plants (WTPs) also have a strong interest in understanding the robustness of their processes/operations on the removal/deactivation of NDMA precursors. Some of the previous studies have shown that NDMA FP changes before and after treatments were negligible with alum (Sacher et al., 2008) and ferric chloride (Knight et al., 2012) in bench-scale experiments. In other studies, an increase in the NDMA FP was reported after conventional clarification (i.e., coagulation, flocculation and sedimentation) compared to raw water (Krasner et al., 2008; Krasner et al., 2012; Sacher et al., 2008; Mitch et al., 2009). Such increases were attributed to the use of flocculation aid polymers during conventional clarification processes. Although other treatment processes (i.e., membrane, powdered activated carbon [PAC] and oxidation) have been examined by other researchers (Mitch and Sedlak, 2004; Pehlivanoglu-Mantas and Sedlak, 2008; Lee et al., 2007; Sacher et al., 2008; Shah et al., 2012; Selbes et al., 2014; Hanigan et al., 2012), the robustness and variability of NDMA precursor removal under dynamic operation of full-scale WTPs have not been fully understood. Therefore, knowledge about the fate of NDMA precursors during water treatment processes under dynamic operational conditions is limited due to insufficient data from long term and systematic studies in the literature.

Considering the effectiveness of oxidants in reducing NDMA formation to various degree (Lee et al. 2007; Charrois and Hrudey 2007; Sacher et al. 2008; Chen and Valentine 2008; Gates et al. 2009; Shah et al. 2012; Selbes et al., 2013) pre-oxidation can be used as an approach to deactivate NDMA precursors before chloramine addition during water treatment. The use of chlorine dioxide (ClO_2) at WTPs has been increasing because ClO_2 oxidation forms significantly lower amounts of regulated THMs and HAAs as compared to chlorination (Blanck, 1979; Zhang et al., 2000; Richardson et al., 1994; Zhang et al., 2000; Gates et al., 2009). Therefore, ClO_2 oxidation may provide an alternative to control NDMA formation. The impacts of ClO_2 on the reduction of NDMA formation potential (FP) have been investigated in a few studies (Lee et al., 2007, Sacher et al., 2008; Shah et al., 2012; Yang et al., 2013), but research on the effectiveness of ClO_2 dose, contact time, oxidation pH on NDMA control is still needed.

The main goals of this study were to (i) monitor NDMA precursors' concentration levels by measuring NDMA FPs in various surface waters (i.e., rivers, lakes/reservoirs) for an extended period of time, (ii) examine the removal efficiency of NDMA FP at different WTPs that are currently complying with Stage 2 Disinfectants and Disinfection By-products Rules (Stage 2 D/DBPR), (iii) investigate the effects of ClO_2 on the removal of NDMA FP at different source waters (e.g., wastewater [WW] vs. low/non-impacted waters) under different oxidation conditions (i.e., pH, oxidant dose), and iv) evaluate the effects of individual vs. integrated oxidation with ClO_2 and Cl_2 at different waters (e.g., WW/polymer impacted vs. low/non-impacted waters) under different oxidation conditions (i.e., pH, oxidant dose). Due to regulatory significance, formation of THMs, ClO_2^- (chlorite) and ClO_3^- (chlorate) was also monitored in selected samples.

CHAPTER TWO

LITERATURE REVIEW

This chapter evaluates the background information on i) the health effects, formation pathways and the occurrence of nitrosamines in drinking waters, ii) sources of nitrosamine precursors and their seasonal/temporal changes in surface waters, and iii) the removal of such precursors during full and bench scale treatment operations under dynamic and controlled operational conditions.

Background

Over 600 DBPs have been reported in simulated laboratory disinfections or disinfected drinking waters, resulting from the use of oxidants, notably chlorine, chloramines, ozone and chlorine dioxide (Bond et al., 2011). Recently, comparison of data from in vitro mammalian cell tests demonstrated that the nitrogenous DBPs (N-DBPs) are far more cytotoxic and genotoxic than carbonaceous DBPs (C-DBPs) (Plewa and Wagner, 2009). Furthermore, nitrosamines, a group of compounds classified as probable human carcinogens in water at concentrations as low as 0.2 ng/L, are associated with a 10^{-6} lifetime cancer risk (USEPA, 2002). Among N-DBPs, nitrosamines became one of the hot topics in drinking water science when they were detected in tap waters (Nawrocki and Andrzejewski, 2011).

The key factors promoting the formation of nitrosamines in drinking water are mainly associated with chloramination of amine precursors present in drinking water (Choi and Valentine, 2002a, b; Mitch et al., 2003; Charrois and Hrudey, 2007; Nawrocki and Andrzejewski, 2011; Russell et al., 2012). Furthermore, the presence of amine based polymers and/or treated wastewater (WW) derived precursors have been shown to increase nitrosamine formation levels (Sacher et al., 2008) in the distribution systems, and the concentration of nitrosamines also increased with distance from the water treatment facility due to the long contact time with chloramine species (Wilczak et al., 2003; Sacher et al., 2008; Bond et al., 2011).

NDMA Formation Mechanisms

During chloramination, monochloramine (NH_2Cl) or dichloramine ($NHCl_2$) reacts with the dimethylamine (DMA) moiety of amine precursors forming chlorinated unsymmetrical dimethylhydrazine (UDMH-Cl) intermediate and subsequent oxidation to NDMA (Schreiber and Mitch, 2006b; Shah and Mitch, 2012). Since the nitrosation pathway, which is an alternative NDMA formation mechanism, occurs most rapidly at low pH values (i.e., ~3.5) and the rate of nitrosation is slow at neutral and alkaline pH, the UDMH pathway has been used to explain the NDMA formation in drinking water.

In this mechanism, $NHCl_2$ is the responsible chloramine species and dissolved oxygen plays an important role in the formation of NDMA (Schreiber and Mitch, 2006b). That is, an initial nucleophilic substitution reaction between $NHCl_2$ and DMA forms chlorinated 1,1-dimethylhydrazine (UDMH-Cl) which undergoes a nucleophilic substitution reaction with hydroxide to form hydroxylated UDMH, which is then be oxidized by oxygen species (i.e., dissolved O_2 or superoxide) to form NDMA. However, the reported NDMA molar yields for the reaction of DMA during chloramination were less than 3% (Mitch and Sedlak, 2004; Schreiber and Mitch, 2006b; Sacher et al., 2008; Farréa et al., 2011). The DMA-$NHCl_2$ pathway resulting in such low NDMA conversion yields, however, does not explain high (~80-90%) molar NDMA yields from some model precursor compounds (e.g., ranitidine). Selbes et al. (2013) reported that NDMA yields during chloramination were closely associated with the chemical structure of tertiary amine precursor compounds and that both stability and electron distribution of the leaving groups of tertiary amines are important factors influencing the reactivity of NDMA precursors. Furthermore, many studies have indicated the importance of pH on NDMA formation with the highest NDMA yields observed with some anthropogenic compounds at pH 7.5-8.5, a practically relevant pH range for drinking water treatment (Mitch and Sedlak, 2002a; Schreiber and Mitch, 2005, 2006b; Sacher et al., 2008; Valentine et al., 2006; Park et al., 2007).

A few studies have investigated the influence of temperature on NDMA formation, and the results are not consistent. Most chemical reactions, including nitrosamine formation, tend to proceed faster with increasing temperature. Valentine et al. (2006) while examining 21 water utilities in North America observed higher levels of NDMA formation in November than August. This was attributed to the more preservation of NDMA precursors in winter than summer months. Krasner et al. (2011) examined the effect of temperature on a wastewater impacted water source at pH 7.0, and reported higher NDMA formation at 25°C than 5°C, while the opposite temperature effect was observed at pH 8.0. Chang et al. (2011) investigated NDMA formation from different precursors at three different temperatures. For DMA, NDMA formation was about the same at 25°C and 35°C, which was higher than at 15°C. For benzalkonium chloride, no temperature effect was observed from 15° to 35°C. For 3-(N,N-dimethyloctylammonio) propanesulfonate, highest NDMA formation was obtained at 25°C which was higher than both at 15° and 35°C.

Occurrence of NDMA

In 1989, NDMA was reported for the first time in drinking water in Ontario, Canada (Jobb et al., 1994). As indicated before, nitrosamines have been detected mostly in the chloraminated drinking water distribution systems. Among such nitrosamines, NDMA was the most commonly detected nitrosamine species (Bond et al., 2011; Wang et al., 2011; Malcolm Pirnie, Inc., 2011; Russell et al., 2012; Woods and Dickenson, 2015). Researchers have found that the NDMA precursor concentration of 50 ng/L typically results in the formation of more than 10 ng/L of NDMA after chloramination under typical drinking water treatment conditions (Gerecke and Sedlak, 2003; Faree et al., 2011).

In the US, the most comprehensive nitrosamine data set in drinking water has been obtained during UCMR 2 monitoring (Russell et al., 2012). NDMA was the dominant nitrosamine species observed by far with concentrations ≥2 ng/L at 25% of the systems monitored. Similar observation were reported in one another study where 45%, 12% and 2% of the chloramine plants had an annual average of ≥2 ng/L, ~10 ng/L and ~50 ng/L of NDMA concentrations, respectively (Malcolm Pirnie, Inc., 2011). Based upon those comprehensive studies i) the highest NDMA concentrations (i.e., >50 ng/L) have been observed at water utilities using chloramines (especially as the primary disinfectant and with long contact times), amine-based polymers (poly (diallyldimethylammonium chloride [polyDADMAC] or poly (epichlorohydrin dimethylamine) [polyamine]), with source waters influenced by agricultural runoff and wastewater discharges, and ii) if a maximum contaminant level (MCL) of 10 ng/L is set for NDMA, ~12-20 % of water systems using chloramines would be directly impacted assuming compliance is based on a locational running annual average (LRAA).

Source of NDMA Precursors

Amines which are possible precursors of NDMA are released from various anthropogenic sources (Sacher et al., 2008; Schreiber and Mitch, 2006a; Bond et al., 2011; Shen and Andrews, 2011; Le Roux et al., 2011; Selbes et al., 2013), in contrast with the regulated THMs and HAAs, for which natural organic matter (NOM) constitutes the main precursor pool. Higher NDMA FPs in WW-impacted water sources with higher pharmaceutical levels (e.g., primidone, carbamazepine) and boron support this assessment (Schreiber and Mitch, 2006a). None of the general water quality chemical parameters (e.g., pH, total organic carbon [TOC], ultraviolet absorbance at 254 nm [UV_{254}], alkalinity, ammonia [NH_3], nitrite [NO_2^-] and nitrate [NO_3^-]) correlated well with the NDMA FP (Sacher et al., 2008). Although an organic nitrogen precursor is required for NDMA formation, there has been no strong correlation with dissolved organic nitrogen (DON) concentrations in natural waters (i.e. wastewater and/or agricultural runoff).

To date, several studies have investigated the formation of NDMA from DMA (Mitch et al., 2003), tertiary and quaternary amines with DMA functional group (Lee et al., 2007; Kemper et al., 2010; Shen and Andrews, 2011), NOM and fractions of NOM (Gerecke and Sedlak, 2003; Mitch and Sedlak, 2004; Chen and Valentine, 2007; Dotson et al., 2007; Krasner et al., 2008), polyelectrolytes and ion-exchange resins used in water and wastewater treatment plants (Gough et al., 1977; Kimoto et al., 1980; Najm and Trussell, 2001; Kohut and Andrews, 2003; Wilczak et al., 2003; Mitch and Sedlak, 2004; Nawrocki and Andrzejewski, 2011), fungicides, pesticides, herbicides (Graham et al., 1995; Chen and Young, 2008; Schmidt and Brauch, 2008; Shen and Andrews, 2011), pharmaceuticals, cosmetics (Sacher et al., 2008), wastewater effluent-derived organic matter (EfOM), soluble microbial products (SMPs) resulting from biomass decay and substrate metabolism, and proteins (Barker and Stuckey, 1999; Nawrocki and Andrzejewski, 2011).

Treatment and disinfection processes at wastewater treatment plants (WWTPs) have been found to significantly influence the release of NDMA precursors and NDMA in surface waters (Krasner et al., 2009, 2013). Specifically, complete nitrification reduced NDMA precursors and subsequent NDMA formation via chloramines disinfection. Photolysis decreased NDMA itself in surface waters, while NDMA precursors remained relatively stable (Pehlivanoglu-Mantas and Sedlak, 2006).

Lately, it has also been shown that treated municipal wastewater discharges increased from 1980 to 2008 in some of the US surface waters (Rice et al., 2013), However, the impact of treated WW effluent(s) downstream of discharge points seems site-specific, because it depends on the type and degree of wastewater treatment, the amount of dilution, the travel time between the discharges and water intakes, and the degree of nitrosamine precursor removal or NDMA formation at treatment facilities.

Another important source of nitrosamine precursors is amine-based polymers used as coagulants and coagulant aids in water treatment operations (Krasner et al., 2013). A recent survey indicated that 41% of surface water utilities used polymers in treatment operations, with larger systems using them more frequently (USEPA, 2009). However, the number may be higher because US polymer suppliers reported that 80% of utilities used polymers as a blend with coagulant, of which they may be unaware (Malcolm Pirnie, Inc., 2011). Certain treatment polymers contribute to NDMA formation; these include aminomethylated polyacrylamide [Mannich polymer], polyamine and polyDADMAC (Kohut and Andrews, 2003; Wilczak et al., 2003; Najm et al., 2004; Park et al., 2007; Park et al., 2009). NDMA FPs from these polymers were on the order of Mannich >> polyamine > polyDADMAC > cationic polyacrylamide. Decreasing polymer dose, chloramine dose, and chloramine contact time decreased NDMA formation (Wilczak et al., 2003; Mitch and Sedlak, 2004; Park et al., 2009). Significant NDMA reductions were observed at some Canadian water treatment facilities when the use of amine-based polymers were discontinued (Andrews and Taguchi, 2000; Najm and Trussell, 2001).

The Seasonal and Weather Related Patterns of NDMA FP in Surface Waters

Until this work, there has been only a few studies with limited focus and sampling events conducted to examine the temporal variations of the NDMA and other nitrosamines precursors in natural waters. While studying the contributions of wastewater effluents to DBP formation, Krasner et al. (2008) investigated the FPs of several classes of C-DBPs and nitrosamines in water samples collected from the South Platte River watershed area located in US in February and September, 2004 and April, 2005. Observed NDMA FP tended to increase with increasing dissolved DON, however, the correlation between NDMA FP and DON was not strong. Mitch et al. (2009) investigated 11 water treatment plants (WTPs) and their associated source waters in the summer and fall of 2006 (each plant was sampled once) for the occurrence of several C-DBPs and N-DBPs as well as their precursors. To evaluate year-to-year variations, a follow-up survey was conducted in 2007 (spring, summer, and fall) for these 11 sites plus 5 other plants. Their sampling strategy was designed to demonstrate the impact of wastewater effluents and algal bloom events. Thus, water samples rich in DON contents were obtained and analyzed. No correlation was found between NDMA FP and DON, which is similar to the results obtained by Krasner et al. (2008), even though different water samples from different sources were examined. Mitch et al. (2009) hypothesized that DON contributions from algae and other sources would confound any association between DON and NDMA FP. Amino acids are an important component of DON, but no significant correlation was observed between total amino acids and dissolved organic carbon (DOC) or DON, suggesting that DON composition is site-specific. A few more studies have investigated seasonal effects on the NDMA precursors and evaluated possible relationships between NDMA precursors and water quality parameters (Aydin et al., 2012; Valentine et al., 2006). However, seasonal patterns of NDMA precursors were not scrutinized thoroughly and no strong correlations between NDMA FP and other factors were found due to insufficient sample collection for limited time periods. Although previous research has provided some useful information on the NDMA precursors in source waters and drinking water treatment plants, comprehensive studies detailing the effect of dynamic events in watersheds on the occurrence and reactivity of NDMA and other nitrosamine precursors were missing from the literature.

Removal of NDMA Precursors

The removal of precursors is a more beneficial and effective approach than the removal of NDMA after formation in distribution systems. In this section, the effect of pre-oxidation and selected treatment processes on the removal of NDMA precursors will be reviewed.

In general, <10% of NDMA FP removal was observed during alum or ferric chloride clarifications without pre-oxidation (Sacher et al., 2008; Knight et al., 2012). However, it has been also observed that the level of NDMA FP from surveyed plants that curtailed the application of chlorine or chloramines was higher after coagulation, most likely due to the use of certain types of polymers (Krasner et al., 2008; Sacher et al., 2008; Mitch et al., 2009; Krasner et al., 2012). Coagulation was not effective in removing nitrosamine precursors (e.g., specifically, DMA, diethylamine, morpholine, and piperidine) and some selected free amino acids (Pietsch et al., 2001; Bond et al., 2010). Krasner et al. (2008) evaluated the effect of powdered activated carbon (PAC) application on NDMA precursors` removal in a full scale plant. The removals reached 82% when PAC dose was ~50 mg/L. Sacher et al. (2008) performed laboratory-scale adsorption experiments with PAC (F300) using surface waters. The removal of NDMA FP increased to 90% with increasing PAC doses (1-100 mg/L). Hanigan et al. (2012) reported that a virgin, high performance powdered bituminous-based activated carbon at 3 mg/L application dose removed 40% of NDMA FP in a secondary wastewater effluent. PAC was effective on the removal of wastewater and polyamine derived precursors, while the effect was negligible for the polyDADMAC derived precursors. The dose of PAC was the main factor to increase the removal of NDMA precursors.

Pre-oxidation prior to chloramination can be an effective means of controlling NDMA formation by deactivating precursors. Some of the early studies have shown that NDMA precursors can be deactivated by oxidation with chlorine (Cl_2), ClO_2, and ozone (O_3) (Charrois and Hrudey, 2007; Lee et al., 2007; Chen and Valentine, 2008), while the effect of UV was low compared to HOCl and O_3 (Zhao et al., 2008). It has been reported that an appreciable amount of NDMA precursor was deactivated with only Cl_2 addition for a short contact time (e.g., $\geq$4 minutes) (Chen and Valentine, 2008). Shah et al. (2012) observed that chlorination with the Ct (oxidant concentration × contact time) value of 37 mg*min/L reduced the NDMA formation up to 80% during subsequent chloramination, and further increases in Ct did not result in additional reduction.

Lee and von Gunten. (2010) have shown that Cl_2 and O_3 reacted with only deprotonated amines indicating that an increasing oxidation pH may lead to increases in the deactivation effect of those oxidants. Unlike chlorination or ozonation, however, ClO_2 oxidation may have both positive and negative impacts on the formation of NDMA during subsequent chloramination (Lee et al., 2007; Sacher et al., 2008; Shah et al., 2012). However, some of the literature observations suggested that ClO_2 has the tendency to reduce the NDMA formation in wastewater impacted waters (Shah et al., 2012; Yang et al., 2013), nonetheless, it was difficult to draw general conclusions since different type of waters as well as experimental conditions have been used in these studies. It has also been shown that ClO_2 reaction rates with amines increased with increasing pH, and the reaction rates were accelerated with neutral tertiary amines (Lee et al., 2007; von Gunten et al., 2010). On the other side, the effect of oxidation temperature was limited at pH 7.0, while the deactivation effect of Cl_2 decreased at low temperature (i.e., 5 ^{o}C) and high oxidation pH (i.e., ≥8.0) (Krasner et al., 2012a, 2012b, 2015).

It has been reported that microfiltration and ultrafiltration membranes were not effective on the removal of NDMA precursors (Pehlivanoglu-Mantas and Sedlak, 2008; Krauss et al., 2010), while nanofiltration (NF) and reverse osmosis (RO) membranes achieved NDMA FP removals of 76-98% (Miyashita et al., 2009) and >98% (Krauss et al., 2010), respectively. In addition, the bulk portion of NDMA precursors has been known to consist of small molecular weight compounds (Mitch and Sedlak, 2004; Pehlivanoglu-Mantas and Sedlak, 2008), thus these precursors may pass through 3000 Dalton (Da) ultra-filters.

CHAPTER THREE

OBJECTIVES AND APPROACHES

Previously, many researchers have provided some useful information on the occurrence of NDMA precursors in surface waters and their removal during water treatment. However, comprehensive studies detailing the effect of dynamic events in watersheds and the physical characteristics of watersheds on the occurrence and reactivity of NDMA precursors in source waters, and their fate during water treatment processes under dynamic operational conditions are limited due to limited data from long term and systematic monitoring studies.

In terms of NDMA control in drinking water, observations in literature suggest that ClO_2 oxidation before chloramination may reduce NDMA formation in WW-impacted waters, and ClO_2 reaction rates with amine precursors increase with increasing oxidation pH (Chapter Two). Therefore, it was hypothesized that deactivation of NDMA precursors with ClO_2 oxidation with pH adjustment before chloramination can be an effective way to control NDMA formation in WW-impacted source waters.

Most previous studies evaluating the removal of NDMA precursors were conducted by using either Cl_2 or ClO_2. However, the effects of mixed oxidants on the removal of NDMA precursors have not been evaluated. Since the WW effluents and polymers used during clarification process are the main two sources of NDMA precursors (Chapter Two), it was also necessary to evaluate the effect of Cl_2 and/or ClO_2 oxidation on the WW- and polymer-impacted waters.

The main objectives in this study were to investigate:

1. the NDMA FP levels in various source waters (i.e., rivers and lakes/reservoirs) and their temporal (seasonal and episodic events) variations,
2. the removal of NDMA FP at full scale WTPs and the occurrence of NDMA in distribution systems,
3. the effect of ClO_2 oxidation on the removal of NDMA FP in WW-impacted waters and the effect of oxidation pH and
4. the effect of integrated oxidation with ClO_2 and Cl_2 on the removal of NDMA FP.

Approaches

Objective 1: **To investigate the NDMA FP levels in various source waters (i.e., rivers and lakes/reservoirs) and their seasonal/temporal variations.**

Approach: Twelve different source waters including rivers, lakes/reservoirs located on different watersheds in the southeastern US were selected. Source waters were categorized based on i) their hydrological characteristics, and ii) anthropogenic impact levels. Water samples were collected on a monthly basis for February 2012-August 2013 and then quarterly until February 2014. NDMA occurrences and FP levels were monitored along with basic water characteristic parameters such as DOC, UV, DON, bromide, and boron. THM occurrences and FP levels were also measured due to their current regulatory importance in the US and for the purpose of comparison (**Figure 3.1**). Sucralose, a widely used artificial sweetener was measured in selected months to assess the impacts of wastewater effluents or other anthropogenic activities on source waters.

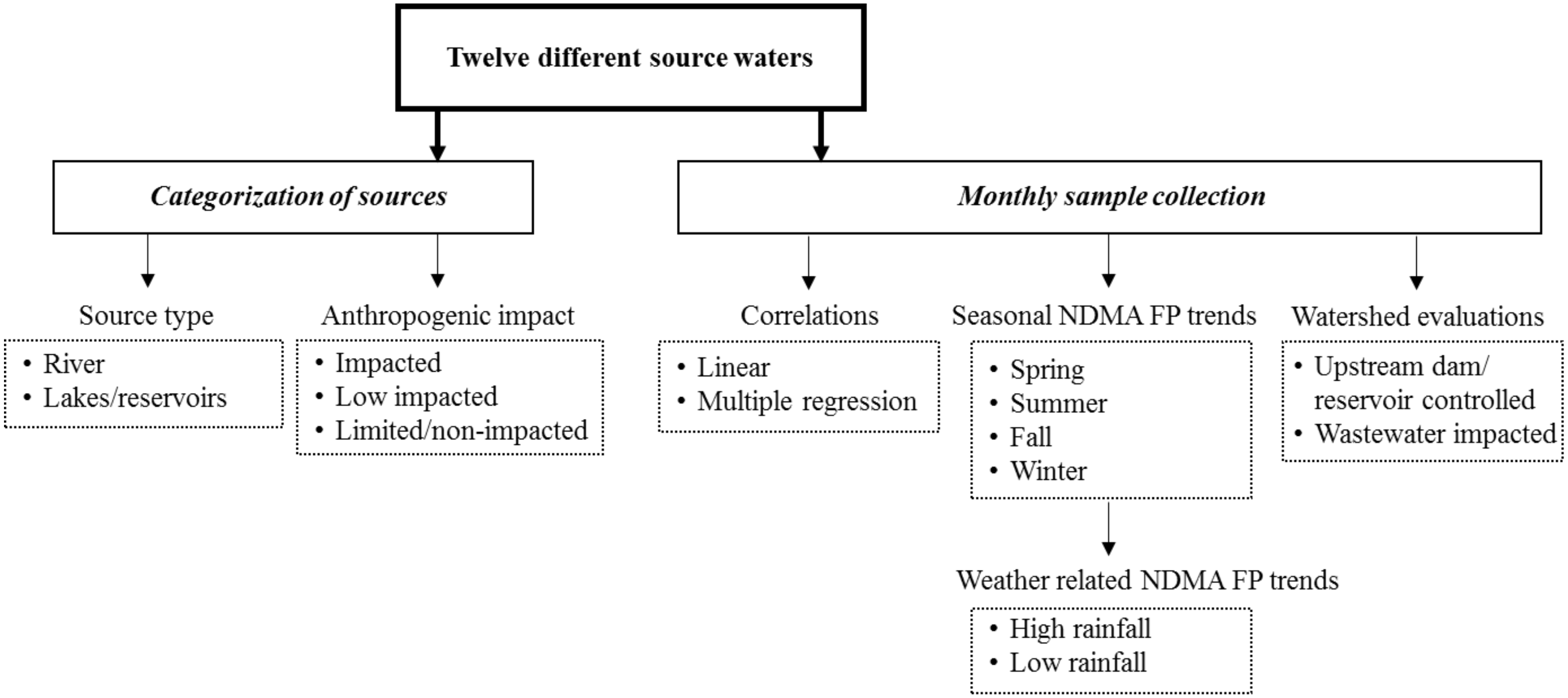


Figure 3.1. Approach for Objective 1.

For each source water, i) linear correlations and multiple regression analysis were conducted for NDMA FP vs. other water quality parameters (i.e., THM FP, DOC, specific ultraviolet absorbance [$SUVA_{254}$], DON, bromide, boron, and sucralose), ii) monthly measured NDMA FPs were plotted for four different seasons; spring (March-May), summer (June-August), fall (September-November), and winter (December-February).

In addition, daily precipitation data for the source water areas near the sampling sites and river flow information were obtained from drinking water treatment plants and US Geological Survey (USGS) stations, respectively, to investigate the impact of rainfall on the changes of NDMA FP. Based on the data obtained, the historical regional average precipitation in the project area (1961-1990) was 49.6 inch/year or 0.13 inch/day. During the study period, cumulative rainfall data were plotted for each source water and NDMA FPs were examined for distinctively high rainfall periods (i.e., above the average) and low rainfall periods (i.e., below the average).

To explore potential major sources of NDMA precursors, additional samples were collected across the two different watersheds including WW- impacted and upstream dam controlled rivers on a monthly basis for more than 6 months. NDMA FP, and THM FP, and selected water quality parameters were measured in all the samples.

Objective 2: To investigate the removal of NDMA FP at full scale WTPs and the occurrence of NDMA in distribution systems.

Approach: To evaluate the removal efficiency of NDMA precursors by each treatment processes and the occurrence of NDMA in distribution systems, samples were collected from influent (i.e., raw water), clarifier or dissolved air flotation (DAF) effluents (only from WTP 9), after post oxidation (primary) disinfection with Cl_2 and/or ClO_2 (i.e., point of entry [POE]), and the longest point in the distribution systems of nine different WTPs. A sampling campaign was conducted on a monthly basis for February 2012-August 2013 from all WTPs, and then on a quarterly basis until February 2014 from the selected WTPs. Occurrence and FP levels of NDMA and THM were measured (**Figure 3.2**). The effects of alum clarification, PAC application, pre-oxidation with Cl_2 and/or ClO_2 and NH_2Cl (i.e., before conventional treatment), and post oxidation with Cl_2 and/or ClO_2 on the NDMA FP removals were evaluated at the WTPs.

The long term sampling strategy allowed the assessment of the impacts of weather related events (seasonal and episodic) on the NDMA FP removal efficiency. As indicated in Objective one, cumulative rainfall data for each raw water were used to examine the NDMA removals during high (i.e., above the average) and low (i.e., below the average) rainfall periods.

NDMA occurrence levels in distribution systems were monitored monthly by taking samples from each plant effluent and the longest detention time location. In addition, FP tests were conducted with selected samples from the plant effluents (i.e., POE samples) and distribution system locations to examine the conversion of NDMA FP to NDMA occurrence.

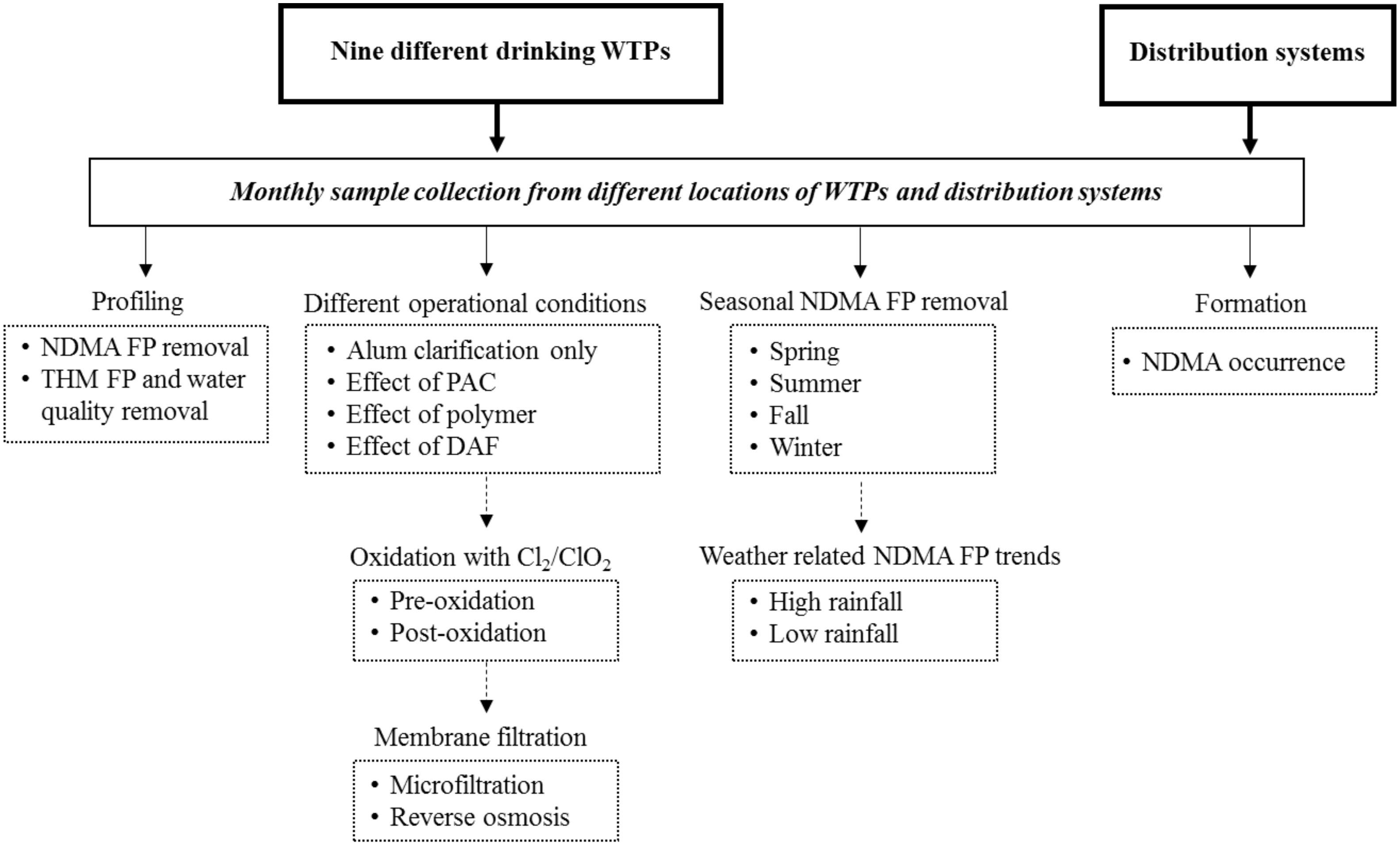


Figure 3.2. Approach for Objective 2.

<u>Objective 3:</u> To investigate the effect of ClO_2 oxidation on the removal of NDMA FP in WW-impacted waters and the effect of oxidation pH.

<u>Approach:</u> Samples were collected from i) the clarifier effluent of a WTP (i.e., after conventional treatment), ii) non-impacted lake water, iii) treated effluents of a municipal WWTPs, and v) upstream (creek) and effluent of another municipal WWTP. Different levels of wastewater impacted samples were prepared in the laboratory by mixing either lake/reservoir or creek water with different amounts of WWTP effluent waters to create 10-50% impacted water samples. Then ClO_2 oxidations were applied to these samples under various oxidation conditions (**Figure 3.3**). To examine the pH effect, experiments were conducted with ClO_2 at pH 6.0, 7.8, and 9.0 (for selected samples) and 1.4 mg/L and 0.7 mg/L (for selected samples) of initial doses for up to 90 min of contact time before NDMA FP tests with chloramines. Similar oxidation tests were conducted followed with uniform formation condition (UFC) tests for selected samples to mimic the NDMA formation in distribution systems at a lower NH_2Cl concentration than the FP test. Furthermore, the effect of i) natural attenuation on the reactivity of ClO_2 towards WW-derived NDMA precursors, and ii) ClO_2 on the removal of THM FPs were also investigated in selected samples.

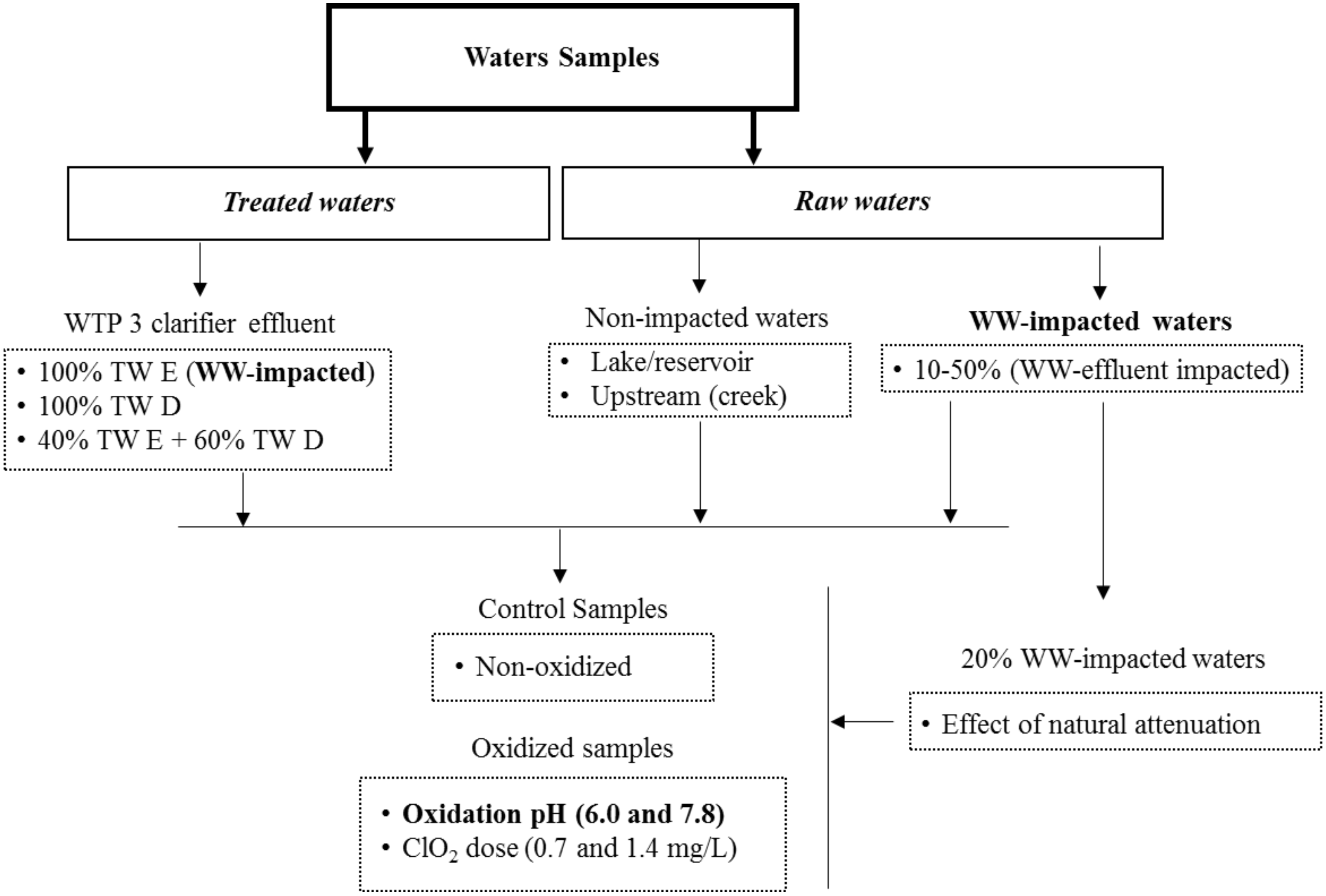


Figure 3.3. Approach for Objective 3.

Objective 4: To investigate the effect of integrated oxidation with ClO_2 and Cl_2 on the removal of NDMA FP.

Approach: A lake water and two municipal WWTP effluent water samples were collected to prepare two 20% WW-impacted samples. Polymer-impacted water samples (0.25 mg/L polyamine, 0.5 mg/L poly DADMAC, and 2.0 mg/L polyacrylamide) were also prepared by spiking pre-determined amount of polymer stock solutions into the lake water samples. (**Figure 3.4**).

The upper limit for the initial dose of ClO_2 was set at 1.4 mg/L to keep ClO_2^- formation under the regulatory limit (i.e., 1.0 mg/L) while the upper limit of free chlorine was set at 2.2 mg/L to minimize the formation of THMs. Lower oxidant concentrations (i.e., initial doses of 0.7 and 1.1 mg/L for ClO_2 and Cl_2, respectively) were also applied to selected samples to investigate the effect of oxidant dose on the deactivation of NDMA precursors and formation of other DBPs (i.e., THM, ClO_2^- and ClO_3^-). Two oxidant contact times (i.e., 10 and 60 min) and two oxidation pH conditions (i.e., 6.0 and 7.8) were tested during the experiments.

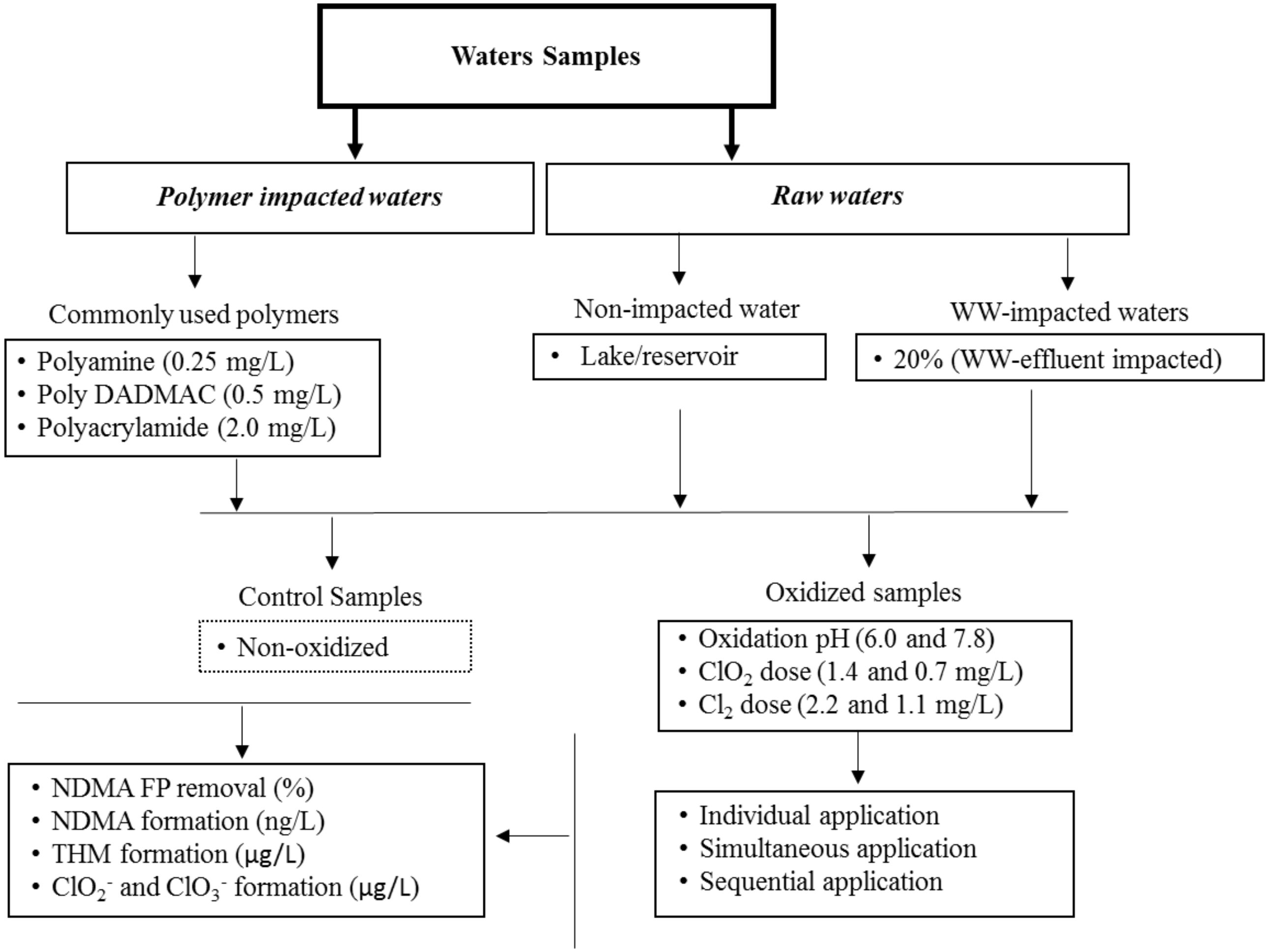


Figure 3.4. Approach for Objective 4.

CHAPTER FOUR

MATERIALS AND METHODS

In this chapter, the detailed description of experimental approaches, materials and methods used in this research is provided. Since different experimental methods were used in different phases of the study, if needed, a short summary of the experimental matrix that is conducted for the particular chapter will be provided in the beginning of the chapters. The methods conducted in this research can be classified in to following categories: i) samples collection, ii) water quality characterizations (i.e., UV_{254}, DOC, DON, NO_2^-, Br^-, NO_3^-, and boron), and iii) analysis of nitrosamines and THMs.

Glassware

All the glassware were cleaned by the following procedure: i) glassware was rinsed with tap water and a detergent, ii) rinsed glassware were sonicated approximately ~20 min with distilled water, and ii) sonicated glass wares were rinsed five times with distilled and distilled deionized water (DDW), respectively. Then the rinsed glassware dried at least 12 hr (103 ºC) inside the oven to avoid any contamination and dust.

Raw and Treated Water Sample Collection

Water samples were collected on a monthly basis for February 2012-August 2013 and then quarterly until December 2014 from all source waters and selected drinking WTPs. Raw water samples were collected from 12 different source waters (3 rivers and 9 reservoirs/lakes) that are serving nine WTPs. Source waters (e.g., SW A, SW B, and etc.) and the WTPs were named (e.g., WTP 1, WTP 2 and etc.) by letters and numbers, respectively (**Table 4.1**). However, no large natural lakes were studied in this work (several have been created for different purposes), the reservoir and lake terms were used based on official names of the source waters.

Table 4.1. Source waters and their served WTPs.

Upstream source (main)	Raw water (intake)	WTP*s*
SW A[a] (river)	SW B (reservoir)	1
	SW C (reservoir)	2
	SWs D[b] (reservoir) and E (river)	3
	SW F (lake)	4
	SW G (river)	5
Mixture of SWs H (reservoir) and SW I (lake)	SW J[c] (river)	6
	SW K (reservoir)	7
	SW L (lake)	8
	Mixture of SWs M (reservoir) and N (reservoir)	*9*

[a]SW A is the common source for the SW B, and SW C that are serving WTPs 2 and 3, respectively. [b]WTP 3 uses two independent sources, and the usage of SW D is more than 90% of total raw water at WTP 3. [c]WTP 6 uses SW J (river) which is the mixture of upstream reservoirs (i.e., SWs H and I).

Detailed watershed evaluations for all source waters and water treatment configurations of WTPs are presented in **Appendix A**. During the study, most of the raw water samples were collected near or from the intakes of served WTPs, and treated water samples were collected from different locations of WTPs (i.e., clarifier effluent and finished water). Surface water samples were used to (i) monitor NDMA precursors' levels by measuring NDMA FPs in various surface waters, (ii) investigate the impacts of seasonal variations and weather events on the NDMA and THM FP at the studied waters.

Raw and treated water samples were used to i) examine the removal efficiency of NDMA FP at full-scale WTPs for an extended monitoring period, and ii) assess the impacts of several operational conditions such as alum clarification, PAC application, pre-oxidation with Cl_2 and/or ClO_2 and NH_2Cl (i.e., before conventional treatment), and post oxidation with Cl_2 and/or ClO_2 on the NDMA FP removals across WTPs, and iii) evaluate NDMA occurrence levels at the distribution system. All WTPs use chloramine as the final disinfectant except for two WTPs using chlorine (i.e., WTPs 6 and 7).

NDMA FP removal efficiencies for conventional clarification and primary disinfection were calculated using following equations;

$$\text{Conventional removal } \% = [(C_{raw} - C_{eff})/C_{raw}] \times 100 \qquad \textbf{Equation 4.1}$$

$$\text{Post-oxidation removal } \% = [(C_{eff} - C_{oxi})/C_{eff}] \times 100 \qquad \textbf{Equation 4.2}$$

where, C_{raw}=NDMA FP (ng/L) in raw water, C_{eff}=NDMA FP (ng/L) in treated water (i.e., clarifier effluent, before filters and any oxidant addition), C_{oxi}=NDMA FP (ng/L) after primary disinfection (i.e., at POE).

Chemical Reagents and Stock Solutions

All chemicals used were purchased from certified vendors. All chemicals used were American Chemical Society reagent grade. Solvents used in the extraction were high purity grades. All stock solutions and buffers were prepared fresh at the time of use, otherwise they were stored in amber borosilicate glass bottles at 4°C. All chemical standards of nitrosamines and THMs are commercially available. Based on the purities of nitrosamines and THMs species provided by manufacturer, stock solutions were prepared by dilution of concentrated stocks. EPA 521 nitrosamine mix (2000 µg/mL of each component, 98.6-99.9%) in methanol, nitrosamine calibration mix of N-nitrosodimethylamine-d_6 (NDMA-d_6, 98%) as a surrogate and N-nitrosodi-n-propylamine-d_{14} (NDPA-d_{14}, 99%) as an internal standard (1000 µg/mL of each in dichloromethane [DCM]) were purchased form Sigma Aldrich and Restek, respectively. Nitrosamine mix (2000 µg/ml of mix) and nitrosamine calibration mix (1000 µg/ml of NDMA-d_6 and NDPA-d_{14}) solutions served as the master stock solutions. They were used to prepare individual 500 µg/L of working nitrosamine mix solution or 400 µg/L of calibration solution. Primary diluted stock (PDS) of nitrosamine stock (~500 µg/L) was prepared by transferring 25 µL of nitrosamine master stock (2000 µg/ml of nitrosamine mix in DCM) to 100 mL of DCM with a micro-syringe. For ~400 µg/L of surrogate and internal standard PDS solution, 10 µL of stock (1000 µg/mL of NDMA-d_6 and NDPA-d_{14} in DCM) was transferred with a micro-syringe to 25 mL of DCM. These PDS solutions in DCM were used to generate calibration curves for each measurement.

Analytical Methods

A summary of the analytical methods used in the study is presented in **Table 4.2**. Detailed information about used analytical methods is provided in the following sections.

NDMA Occurrence

NDMA occurrence was measured for all twelve source waters and samples obtained from selected locations of each WTP. Water samples were collected in 1000 mL amber glass bottles. Sodium thiosulfate (~30 mg) was added into the bottles to quench the residual oxidants and to avoid further formation of NDMA. Samples, in an ice chest, were immediately transferred to the laboratory, and stored in the refrigerator at 4 °C in the dark until analysis.

Table 4.2. Analytical methods and minimum reporting levels.

Parameter	Unit	Measurement method	Equipment	Minimum reporting level or accuracy[a]
Dissolved organic carbon (DOC)[b]	(mg/L)	SM[c] 5310B	TOC-V$_{CHS}$, Shimadzu Corp.	0.1
Dissolved nitrogen (DN)	(mg-N/L)	High temperature combustion	Shimadzu TOC-V$_{CHS}$ & TNM-1,	0.1
UV absorbance[d]		SM 5910	Varian Carry 50	±0.004
Br^- NO_3^- NO_2^-	(µg/L)	USEPA Method 300	ICS 2100, Dionex Corp.	Br^-=10, NO_3^-=15, NO_2^-=20
ClO_2^- ClO_3^-	(µg/L)	USEPA Method 300.1 Part B	ICS 2100, Dionex Corp.	10
pH		SM 4500-H$^+$	VWR Symphony	±0.01[e]
NH_3	(mg/L)	Salicylate Method	HACH Test Kit	0.02
ClO_2	(mg/L)	SM 4500-ClO_2 D	HACH Test Kit	0.05
Nitrosamines[f]	(ng/L)	USEPA Method 521	Varian GC/MS/MS	3.0
THMs[g]	(µg/L)	USEPA Method 551.1	Agilent 6890 GC/ECD,	1.0
Boron	(µg/L)		Spectro ARCOS ICP	1
Sucralose	(ng/L)		LC/MS/MS	25
Free/Combined Chlorine	(mg/L)	SM 4500-Cl F	N/A[h]	0.05

[a]As reported by the manufacturer. [b]Reagent grade potassium hydrogen phthalate was used to prepare external standards. Precision ranged from 0.05 to 0.15 mg/L. [c]Standard methods (SM). [d]Measured at wavelengths of 254 nm using a 1 cm cell. [e]Accuracy (pH units). [f]Solid phase extraction followed by gas chromatography mass spectrometry (GS/MS/MS) analysis. [g]Methyl tert-butyl ether (MTBE) solvent extraction followed by gas chromatography/electron capture detector (GC-ECD) analysis, and detailed info about the THM method is provided in Karanfil et al. (2007). [h]Not applicable. [i]Samples were sent to commercial labs for boron and sucralose measurement.

Dissolved organic nitrogen (DON) were determined by DON=DN – NO_3-N – NO_2-N – NH_4^+-N. DON values only for DIN/DN<60% were reported in this study (Lee and Westerhoff, 2005).

Nitrosamine Formation Potential Test

Formation potential (FP) tests were conducted to determine the maximum formation of NDMA and six other nitrosamines (**Table 4.3**) which provides maximum levels of precursors of measured nitrosamines in a sample after 5 days of reaction time in the presence of excess amount of NH_2Cl. FP tests were conducted for all twelve source waters and samples from selected locations from the treatment plants. Water samples, collected in 1000 mL amber glass bottles, were brought to the laboratory and chloraminated. Twenty mM phosphate buffer was added to each bottle to maintain pH at approximately 7.8.Chloramination was performed by spiking a pre-determined volume of NH_2Cl stock solution to achieve 100 mg/L of initial NH_2Cl as Cl_2 concentration. Each bottle received a stir bar and was filled to be headspace free. After 5 days of incubation at room temperature, samples were taken to measure the residual chloramine species, and quenched with sodium thiosulfate, extracted, and analyzed for NDMA and seven other nitrosamine species.

Nitrosamine Measurements

NDMA and six nitrosamine species (N-nitrosomethylethylamine [NMEA], N-nitrosodiethylamine [NDEA], N-nitrosopyrrolidine [NPYR)], N-nitrosodi-*n*-propylamine [NDPA], N-nitrosopiperidine [NPIP] and N-nitrosodi-*n*-butylamine [NDBA]) were analyzed following USEPA Method 521 (**Table 4.3**). Calibration solutions were prepared from a stock of mixed nitrosamines. Typical calibration curves were generated from at least six standard points (**Figure A.12 and 13**). For the sample analysis, 1000 mL of chloraminated solutions were quenched with sodium thiosulfate. NDMA-d_6 was added to the samples as a recovery standard (surrogate) before extraction. Samples were passed through cartridges pre-packed with 2 g of coconut charcoal purchased from UCT. Prior to sample extraction, cartridges were pre-conditioned with DCM, methanol, and distilled and deionized water (DDW).

Table 4.3. Detection information of nitrosamines on GC/MS/MS.

Nitrosamine species	Molecular weight	Quantification ion	Confirmation ion	Retention time (min)
NDMA	74	75.0	43.3, 47.3	6.0
NDMA-d_6	80	81.1	50.3, 49.3	6.0
NMEA	88	89.0	61.1, 43.2	8.5
NDEA	102	103.1	103.9, 75.0	10.5
NPYR	100	101.1	55.1, 102.1	16.3
NDPA-d_{14}	144	145.2	97.2, 146.3	16.3
NDPA	130	131.2	89.1, 132.1	16.6
NPIP	114	115.1	69.1, 116.2	17.9
NDBA	158	159.1	160.2, 103.1	23.4

After solid phase extraction, cartridges were dried with air, and then eluted with DCM. Eluted samples were passed through a column pre-packed with 6 g of anhydrous sodium sulfate and concentrated to 1 mL under high purity nitrogen gas. The extracts were spiked with NDPA-d_{14} as an internal standard, and analyzed using a Varian GC 3800-MS/MS 4000 equipped with RTX-5MS (Restek 30m × 0.25mm × 0.25μm) column under the chemical ionization mode. The injector temperature program was: initially 35°C held for 0.8 minute, and then increased to 260°C at 200°C/min and held for 2.08 minutes. The column temperature program was: 35°C for 5 minutes, increased to 70°C at 5°C/min, then to 87°C at 3°C/min, then to 120°C at 5°C/min, and then to 250°C at 40/min holding for 2.48 minutes. Nitrosamines are sufficiently thermally stable and volatile for direct analysis by gas chromatography. All samples and blanks were prepared and extracted in duplicates, and then each extract was analyzed on GC/MS/MS with multiple injections.

The detection limits (DL) were estimated for all nitrosamine species by eight consecutive analyses (i.e., one injection per vial for the eight vials prepared) of mixture solutions, which contained approximately 5 ng/L of each nitrosamine compound. The following equation was used to calculate DL:

$$DL=S \times t_{(n-1,\ 1-\alpha)} \qquad \textbf{Equation 4.3}$$

where, S=standard deviation of the replicate analyses, $t_{(n-1,\ 1-\alpha)}$=student-t value for the 1-α with n-1 degrees of freedom (e.g., t (7, 0.99)=2.998 for 8 replicates at the 99% confidence level), n=number of replicates, and α=0.01 (i.e., confidence level 1-α=0.99). In practice, this is the lowest point on the calibration curve that can be quantified. However, the minimum reporting level (MRL) was established at a concentration that is three times the DL. The DL and MRL of nitrosamines determined are presented in **Table 4.4.**

Table 4.4. DLs and MRLs of nitrosamines established at 5 ng/L in DDW.

Nitrosamine	Mean measured (ng/L)	RSD (%)	DL (ng/L)	MRL (ng/L)
NDMA	4.8	5.2	0.7	2.2
NMEA	5.1	5.7	0.9	2.6
NDEA	5.0	4.4	0.7	2.0
NPYR	5.2	4.9	0.8	2.3
NDPA	5.5	5.6	0.9	2.8
NPIP	4.5	6.1	0.8	2.4
NDBA	4.5	6.7	0.9	2.7

Spike recovery experiments were also performed to verify that the employed analytical method would be applicable to other water matrices. This was examined by analyzing spike recoveries of nitrosamine species in two source waters with high $SUVA_{254}$ (3.57 L/mg-m) and relatively low $SUVA_{254}$ (2.29 L/mg-m). Samples were spiked from the mix solution containing 10 ng/L of each nitrosamine species before extraction and analysis. The results are shown in **Table 4.5.**

Table 4.5. Spike recoveries of nitrosamines in high and low $SUVA_{254}$ waters.

		High $SUVA_{254}$ water			Low $SUVA_{254}$ water		
Nitrosamine	Fortified (ng/L)	Mean measured (ng/L)	RSD (%)	Mean recovery (%)	Mean measured (ng/L)	RSD (%)	Mean recovery (%)
NDMA	10	8.85	3.5	87	9.52	5.6	93
NMEA	10	9.10	5.6	89	10.61	4.6	104
NDEA	10	9.01	7.9	89	10.88	6.6	107
NPYR	10	9.40	4.6	93	11.31	3.0	112
NDPA	10	8.64	10.8	85	9.57	10.3	95
NPIP	10	7.59	8.4	75	8.11	10.9	80
NDBA	10	6.34	12.9	63	8.28	12.8	82

Stock Solutions for THMs

EPA 501/601 THM standard mix (2000 µg/mL of each component in methanol, 98-99%) and 1,2-dichloropropane as internal standard were purchased from Supelco and Fluka, respectively. The PDS solution of THM standard mix was prepared in MtBE, 99.8% HPLC grade, Sigma-Aldrich). A micro-syringe was used to transfer 100 µL of THM standard mixture to 20 ml MtBE to produce ~10^4 ppb of stock solution. MtBE solution with internal standard was prepared by injection of 50 µg internal standard in 1 liter MtBE.

THM Occurrence

THMs occurrence was measured for all twelve source waters and samples obtained from selected locations in each treatment plant. Water samples were collected in 125 mL amber glass bottles. Sodium sulfite was added as a quenching agent (i.e., ≥2.25 mg sodium sulfite/mg chlorine) into bottles. Samples in ice were immediately transferred to the lab and stored at 4°C in the dark until analysis.

THM Formation Potential Test

THM FP tests were conducted for all twelve source waters and samples collected from selected locations for each treatment plant. The THM FP test was designed to determine the maximum formation of THM after 5 days of reaction time in the presence of excess chlorine. Twenty mM phosphate buffer was added into each bottle to maintain pH at approximately at 7.8. Each bottle received a stir bar and was filled to be headspace free. The samples were chlorinated (50 mg/L of target concentration) by spiking the required amount of a stock solution (5-6% available free chlorine) to the bottles. After 5 days of incubation time at room temperature, samples were quenched with sodium sulfite (Na_2SO_3). Depending on the measured residual chlorine concentration, sodium sulfite was added in slight excess of the stoichiometric requirement. Twenty mL of samples was transferred into a vial, extracted with MtBE, and analyzed.

THM Measurements

USEPA Method 551.1 for the liquid-liquid extraction and GC measurement was employed with minor modifications to extract and quantify THM. Twenty mL of each sample was transferred to a glass extraction vial, and 8 mL of MtBE with 50 μg/L of 1,2-

dichloropropane as an internal standard was added. Then, 8.5 g of reagent grade anhydrous sodium sulfate (Na_2SO_4) was added to the extraction vial to enhance the partitioning of THM into the organic phase and to reduce the water solubility of MtBE. Extraction vials were closed tightly, laid horizontally on a shaker table, and shaken at 300 rpm for 15 minutes. After shaking, the vials were allowed to settle for at least 10 minutes. Two mL of the upper layer of MtBE was transferred into GC vials for subsequent GC analyses.

An Agilent 6890 GC-ECD with an auto sampler equipped with a Phenomenex ZB-1 column (30m × 0.25mm × 1μm) was used for the determination and quantification of THM. The GC temperature program was: 35°C for 22 minutes, increased to 125°C at 10°C/min holding for 1 minute, and then to 300°C at 30°C/minute holding for 4 minutes. Total run time was 41.83 minutes. The injector and detector temperature were 250°C and 290°C, respectively. Ultra-high purity (99.999%) helium gas and high purity (99.999%) nitrogen gas were used as carrier and make-up gas, respectively. Injection volume was 2 μL and the injection mode was splitless.

DOC and DN Measurements

DOC and DN were measured using a Shimadzu TOC-V_{CHS} high temperature combustion analyzer equipped with a TN (TNM-1) module. DOC standards ranging from 0.2 to 15 mg C/L were prepared by diluting 1000 mg C/L of potassium hydrogen phthalate solution and DN standards ranging from 0.4 to 5 mg N/L were prepared by diluting 1000 mg N/L of potassium nitrate solution. Upon arrival in the laboratory, collected samples were filtered with a pre-washed 0.2 µm Supor® membrane filter (PALL), preserved with hydrochloric acid (HCl) at pH 2.0 or less, and stored in a refrigerator prior to DOC and DN analysis.

DON Determination

DON concentrations were determined by the following equation:

$$DON=DN - NO_3\text{-}N - NO_2\text{-}N - NH_4^+\text{-}N \qquad \textbf{Equation 4.4}$$

It has been reported that when the concentrations of dissolved inorganic nitrogen (DIN) exceed 60% of DN values, DON values become less reliable (Lee and Westerhoff, 2005). Therefore, DON values for DIN/DN<60% were reported in this study.

UV Absorbance

UV absorbance was measured using a Cary 50 UV-Vis spectrophotometer (Varian). Samples were filtered with pre-washed 0.2 µm Supor® membrane filter (PALL). One mL of sample was placed in a quartz cuvette and UV absorbance was measured at 254 nm. The spectrophotometer was zeroed by measuring the absorbance of DDW after several rinses. The performance of the instrument was monitored using total organic carbon standards made with potassium hydrogen phthalate (Standard Method 5910).

Bromide, Nitrite and Nitrate

Bromide, nitrite, and nitrate concentrations were measured using a Dionex DX-600 ion chromatography equipped with an AAES suppressor. The standard solutions were prepared with NaBr (> 99.9%, Sigma), $NaNO_2$ (> 99.9%, Sigma), and $NaNO_3$ (> 99.9%, Sigma). A Dionex AS-23 column coupled with an AG-23 guard column and 9 mM of Na_2CO_3 as an eluent were used for the separation of anions. Samples were filtered with pre-washed 0.2 µm Supor® membrane filter (PALL) and stored in a refrigerator prior to the measurements. The MRL determined using 30-40 µg/L standards with seven consecutive analyses are presented in **Table 4.6.** The MRLs were set at 10, 20, and 10 g/L for bromide, nitrite, and nitrate, respectively.

Table 4.6. Detection limits of bromide, nitrite and nitrate.

	Spiked (µg/L)	Mean measured (µg/L)	RSD (%)	DL (µg/L)	MRL (µg/L)
Nitrite	32.3	33.0	6.1	6.4	19.1
Nitrate	40.5	41.3	2.7	3.5	10.5
Bromide	37.4	36.5	2.9	3.3	9.9

Ammonia

Ammonia concentrations were measured using the salicylate method with HACH reagent kits. Samples were preserved using sulfuric acid at pH 2 or less and stored in a refrigerator until analysis. Before analysis the pH of samples was raised to 6-8 using 1M NaOH solution. Salicylate reagent was added to 10 mL sample, and after 3 minute cyanurate reagent was added. After 15 min reaction time, ammonia in the sample was determined with a HACH DR/820 colorimeter. The method performance was checked regularly by preparing a 0.4 mg/L ammonia solution using a certified ammonia nitrogen standard solution (HACH). Detection limit of this method is 0.02 mg/L.

Free Chlorine and Monochloramine

Chlorine (Cl_2) stock solution was prepared by dilution of sodium hypochlorite solution (5-6 % available chlorine) in DDW. Pre-formed NH_2Cl stock solution was prepared ex-situ by adding Cl_2 stock solution to $(NH_4)_2SO_4$ solution at pH ~9. A slow addition (i.e., drop by drop) is desired to avoid the formation of $NHCl_2$. The Cl_2/N ratio was set at 4:1 by weight to keep under the chlorine breakpoint and to mimic practical applications of water treatment utilities. Chlorine and NH_2Cl concentrations were measured using the N,N-diethyl-p-phenylenediamine (DPD) method (Standard Method 4500).

Chlorine Dioxide Production

ClO_2 stock (~1500 mg/L) was generated by acidifying 15% $NaClO_2$ solution with 6N H_2SO_4 (Jones et al., 2012). The whole system was operated under a vacuum in the hood. The flow rate of sodium chlorite solution was monitored closely because flow rates that were too fast could have resulted in the cold ClO_2 reservoir turning red, which indicates an explosive hazard. The gas bottle was covered in foam as a precaution. If the production system was operating at its optimum, the ClO_2 solution was a yellow color, and progressively became a darker yellow as all the sodium chlorite in the reservoir was reacted. The system was shut-down safely by first disconnecting the gas wash bottles furthest from the vacuum, and then disconnecting bottles carefully in tandem. The vacuum was not turned off until all bottles were disconnected to avoid cross contamination and another explosive hazard.

The ClO_2 stock solution was kept in an amber glass bottle (no air headspace) in the refrigerator and was not stored for more than a month. Chlorine dioxide (ClO_2) was measured using a HACH DR/820 colorimeter with DPD colorimetric test kits according to HACH Method 10126. ClO_2 measurements were performed onsite during the sampling events to determine the residual ClO_2 levels after certain treatment processes. Ten mL of sample was transferred into a vial and 4 drops of glycine (10%) was added to mask the free chlorine. The concentration of ClO_2 was measured after the addition of DPD reagent. DDW was used as a blank for the instrument.

Jar Tests Procedure

Jar tests were carried out using PHIPPS & BIRD™ PB-700™ jar tester equipped with six paddles rotating in a six beakers. The first step of the jar test involved pH adjustment with HCl and NaOH to intended pH (pH~6 and ~7). Then, a pre-determined amount of alum was added to the tested water and mixed rapidly (100 rpm=1 min, and 60 rpm=3 min) to completely dissolve. Then the water was mixed slowly for a longer time period (20 rpm=30 min). During the mixing periods pH changes were kept under control and were recorded at the end of the mixing periods. Finally, the mixer was stopped and the flocs were allowed to settle out (30-45 min), then the samples were collected from mid-point of the beakers and used for FP tests.

Boron

For the boron measurement, approximately 10 mL of filtered source water samples were transferred to disposable tubes, and one drop of nitric acid was added as a preservative. Samples were then sent for analysis, and 12 elements including boron were measured using a Spectro ARCOS ICP. The detection limit of boron was 1μg/L.

Sucralose

Sucralose which is a widely used artificial sweetener was measured to assess the impacts of wastewater effluents or other anthropogenic activities on source waters. One liter of source water samples were shipped to the Southern Nevada Water Authority for analysis. Sodium azide (1 g) was added in the bottles as a preservative. Sucralose concentrations were determined using a LC/MS/MS. The MRL of sucralose was 25 ng/L.

CHAPTER FIVE

NDMA FP CHANGES IN SOURCE WATERS

Introduction and Objectives

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

Therefore, one of the main objectives of this research were to (i) monitor NDMA precursors' levels by measuring NDMA FPs in various surface waters, (ii) examine correlations between NDMA FP and selected water quality parameters, (iii) investigate the impacts of seasonal variations and weather events on the NDMA FP with a comprehensive long term study, and v) examine the effect of watershed dynamics on NDMA FP levels in selected source waters.

Sampling and FP test

Water samples were collected (on a monthly basis for February 2012-August 2013 and then quarterly until February 2014) from 12 different source waters (3 rivers and 9 lakes/reservoirs) located in the southeastern US. Most of the sampling sites were located near or at the intakes of drinking water treatments plants.

For the occurrence of NDMA in the source waters, samples were collected in 1000 mL amber bottles and quenched immediately with sodium thiosulfate (~30 mg), transferred to the laboratory, and stored at 4 ^{o}C until analysis. The FP tests were conducted to measure NDMA precursor concentration levels in collected water samples. To determine NDMA FP levels, samples were collected in 1000 mL amber glass bottles, and brought to the laboratory where phosphate buffer (20 mM) was added to each bottle to maintain pH at 7.8. Then, pre-determined volume of monochloramine (Cl_2:N=4:1) stock solution was spiked in the bottles to achieve 100 mg/L of monochloramine. Each bottle was filled to be headspace free with a sample. After 5 days of contact time at room temperature in the dark, residual chloramines in the samples were quenched with sodium thiosulfate, extracted, and analyzed using GC/MS/MS.

For the purpose of comparison, the occurrence and FP of THM were also measured with concurrently collected samples. For the occurrence of THM, samples were collected in 125 mL amber bottles and quenched immediately with sodium sulfite (≥2.5 mg). THM

FP tests were conducted in the presence of 50 mg/L of chlorine at pH 7.8 for 5 days contact time, and then THM samples were extracted and analyzed using GC/ECD. THM FP was included in the study due to its current regulatory importance in the US and for the purpose of comparison.

Analytical Methods

NDMA and other nitrosamines were analyzed following USEPA method 521 (USEPA, 2004) using Varian GC 3800-MS/MS 4000 under CI mode equipped with a RTX-5MS (Restek 30 m x 0.25 mm x 0.25 mm) capillary column. THMs were measured following USEPA Method 551.1 using Agilent 6890 GC-ECD equipped with a Phenomenex ZB-1 column (30 m x 0.25 mm x 1 mm). Analysis of THMs and NDMA has been described in detail elsewhere (Uzun et al., 2015). Concentrations of chlorine and chloramine reported as free and combined chlorine, respectively, were determined following Standard Method 4500-Cl F (APHA/AWWA/WEF, 2005). Analytical methods and their MRLs for water characterization parameters (e.g., DOC, $SUVA_{254}$, DON, bromide, boron, and sucralose) are given in **Table 4.2.**

Results and Discussion

Source Water Categorization and General Water Quality Parameters

Observed average values of the general water quality parameters over two years of the monitoring period at the 12 independent source waters are summarized in **Table 5.1.** The results indicate that the source waters encompass a wide range of values for DOC, DON, $SUVA_{254}$, bromide, boron and sucralose (i.e., 1.1-9.7 mg/L, 0.1-0.4 mg/L, 1.3-4.3 L/mg-m, <MRL-190 µg/L, <MRL-52 µg/L, and <MRL-1000 ng/L, respectively).

Relatively high and variable bromide concentrations in SW A, D, and G were linked to the occasional use of bromine compounds for mercury emission control at the upstream coal-fired power plants. For selected samples collected in August 2012, April and November 2013, sucralose, an artificial sweetener, was analyzed as an indicator for anthropogenic influences on source waters (Loos et al., 2009; Mead et al., 2009; Scheurer et al., 2009; Buerge et al., 2009; Ferrer and Thurman, 2010; Torres et al., 2011; Mawhinney et al., 2011).

Table 5.1. Selected water quality parameters of 12 source waters*: Nov. 2011-Dec. 2014 (average ± standard deviation).

Sources	Served WTPs	DOC (mg/L)	DON (mg/L)	$SUVA_{254}$ (L/mg-m)	Bromide (µg/L)	Boron (µg/L)	Sucralose** (ng/L)
SW A	WTP 1 and 2	4.5±1.7	0.3±0.1	3.3±0.7	114±69	17±4	363±65
SW D	WTP 3	5.4±1.0	0.3±0.0	3.3±0.6	190±135	52±15	733±244
SW E		9.7±4.3	0.4±0.1	4.3±0.5	36±10	17±6	133±32
SW F	WTP 4	3.1±0.5	0.2±0.1	1.6±0.4	28±10	18±3	737±135
SW G	WTP 5	3.0±0.8	0.2±0.1	2.8±0.5	128±103	26±10	753±186
SW H	WTP 6	3.6±0.9	0.3±0.1	4.0±1.1	16±7	<MRL	<MRL
SW I		2.8±0.6	0.3±0.1	3.3±1.7	17±7	<MRL	N/M
SW J		2.6±0.6	0.3±0.1	3.7±1.4	18±7	<MRL	64±11
SW K	WTP 7	2.4±0.6	0.3±0.1	2.5±0.5	28±10	<MRL	80±2
SW L	WTP 8	1.1±0.1	0.1±0.1	1.3±0.4	10±6	<MRL	36±13
SW M	WTP 9	1.3±0.2	0.1±0.1	2.1±0.6	<MRL	<MRL	<MRL
SW N		1.3±0.2	0.1±0.0	1.3±0.4	<MRL	<MRL	<MRL

All source waters were named with letter (e.g., SW A, SW D and etc.)
MRL: Minimum reporting level, N/M: Not measured,
*****All values were measured or determined with samples filtered using a pre-washed 0.2 µm membrane filter.
****** Measured only in Aug 2012, Apr and Nov 2013.

Boron concentrations were also measured to assess the impacts of WW effluents on source waters since boron is not effectively removed by WWTP processes (Schreiber and Mitch, 2006). The highest boron levels were observed in SW D (average 57 mg/L) followed by SW G (average 28 mg/L). Boron concentrations did not correlate well with bromide levels at each source water except for SW D (R^2=0.59). Relatively high sucralose levels (average>100 ng/L) in SW A, D, E, F, and G indicated some anthropogenic impacts on these sources. These sources had also higher average boron levels. Moderate sucralose levels (average 50-100 ng/L) were observed in SW J and K, while low concentrations (average<50 ng/L) in SW H, L, M, and N indicate that these sources are less or not impacted by wastewater effluents. There is no established criteria to classify the surface waters based on sucralose levels (**Table B.1**); therefore for this study the following categorization was developed and used to differentiate source waters: (i) anthropogenically impacted sources (sucralose>100 mg/L) [SW A, D, E, F, and G], (ii) anthropogenically low impacted sources (50>sucralose>100 ng/L) [SW J and K], and (iii) limited/non impacted sources (sucralose<50 ng/L) [SW H, L, M, and N].

Relatively elevated sucralose levels (>300 ng/L) in SW A, SW D, SW F, and SW G indicate that there were some anthropogenic impacts, which are likely from wastewater treatment plant effluents, on these sources. Moderate levels (50-170 ng/L) were observed in SW E, SW J, and SW K, and low sucralose concentrations (50 ng/L or less) in SW H, SW L, SW M, and SW N indicate that those sources are classified as limited impacted.

There was a fairly positive linear correlation between boron and sucralose with R^2=0.69 and slope=0.037 (**Figure B.1).** Therefore, boron results were used to estimate possible impacts of wastewater effluents or other anthropogenic activities on the source waters when sucralose data were not available.

Nitrosamine FPs of Source Waters

Six other nitrosamines (i.e., NDBA, NDEA, NDPA, NMEA, NPIP, and NPYR) were also measured for approximately nine months along with NDMA for the occurrence and FP tests. No nitrosamine occurrence was found in 12 source waters, but some nitrosamines species were detected after FP tests. Average concentrations of nitrosamine species are plotted as shown in **Figure 5.1.** The FP levels of NDPA were below the detection limits in all samples. NDMA was the most frequently detected and dominant species followed by NPYR (3-9% of the total nitrosamines). This trend is consistent with the nationwide nitrosamine occurrence data collected under the UCMR 2 where NDEA, NPYR, NDBA, and NMEA have been also detected over the MRL as well as NDMA (Russell et al., 2012). The contributions of NDBA, NDEA, NMEA, and NPIP to the total nitrosamines measured in the 12 different source waters were only 0-6%. For SW A other nitrosamines accounted for about ~24% of the total nitrosamines. However, for the other source waters, approximately 10% of contributions were made by other nitrosamines. Since NDMA was by far the dominant nitrosamine species observed in this and other studies (e.g., Russell et al., 2012), the majority of discussion in this chapter focused on NDMA.

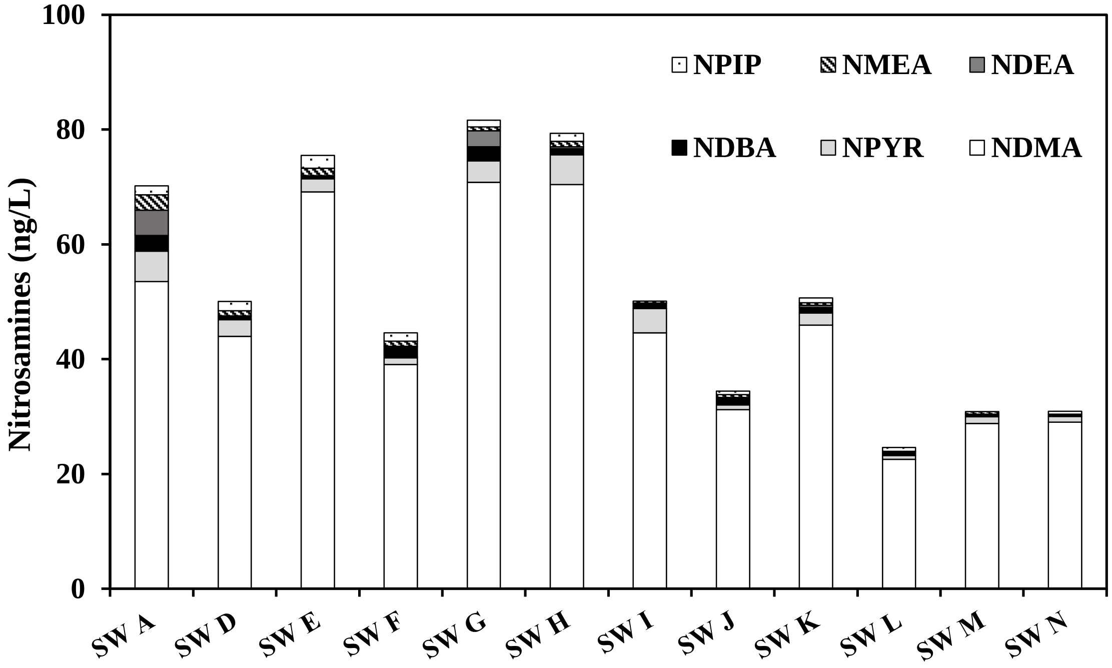


Figure 5.1. Distributions of nitrosamine species in source waters. NDPA was not detected.

Formation Potential Levels of NDMA and THMs

To examine the occurrence of NDMA precursors in the source waters, samples were collected and analyzed on a monthly basis for all source waters from Apr 2012-Aug 2013 period and on a quarterly basis between Aug 2013 and Dec 2014. Samples were also collected for the regulated THMs for comparison purpose during the same periods.

The concentrations of NDMA and THMs were always below the detection limits. FP tests, as described previously, were conducted to determine the precursor concentration levels in source waters. **Figure 5.2** shows the legend for the box-and-whisker plot. The results of NDMA FP and THM FP were organized for rivers and lakes/reservoirs and presented in **Figures 5.3** and **5.4.**

The NDMA FP concentrations were grouped in the following three categories based on the median values:

≥60 ng/L: SW E, SW G
25-59 ng/L: SW A, SW D, SW F, SW H, SW I, SW J, SW K
≤24 ng/L: SW L, SW M, SW N

The THM FP concentrations of the same water samples were also grouped in three categories based on the median values:

>400 µg/L: SW D, SW E, SW H
150-400 µg/L: SW A, SW F, SW G, SW I, SW J, SW K
<150 µg /L: SW L, SW M, SW N

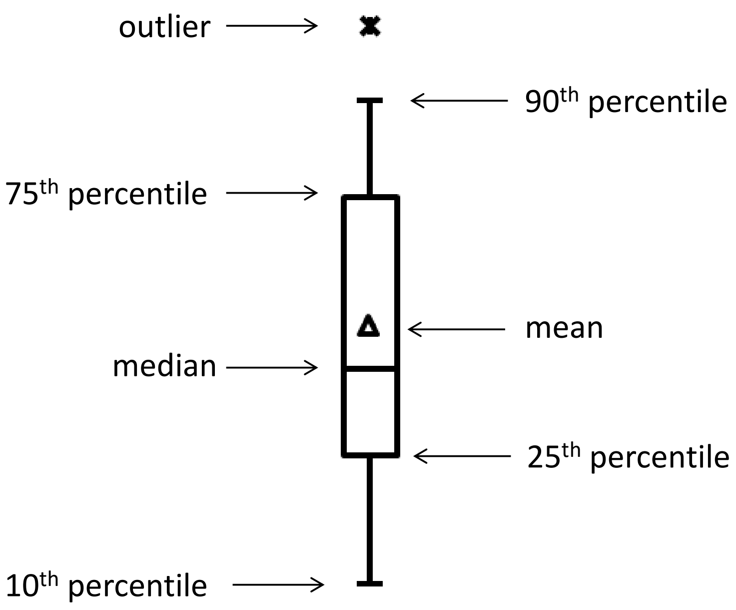


Figure 5.2. Legend for box-and-whisker plot.

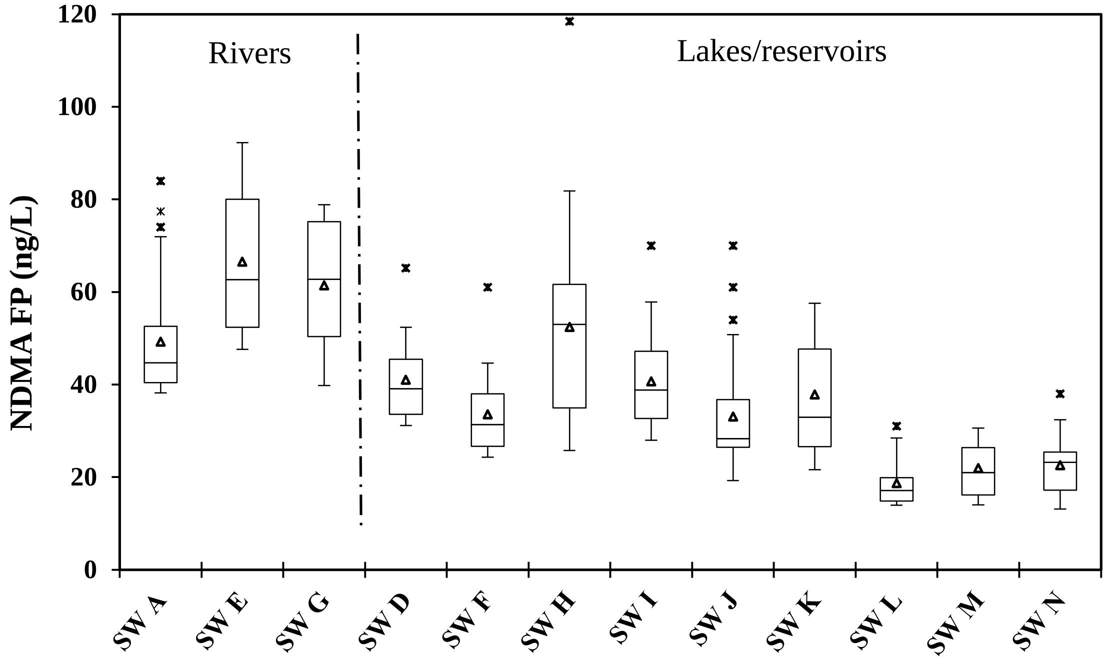


Figure 5.3. NDMA formation potential of source waters.

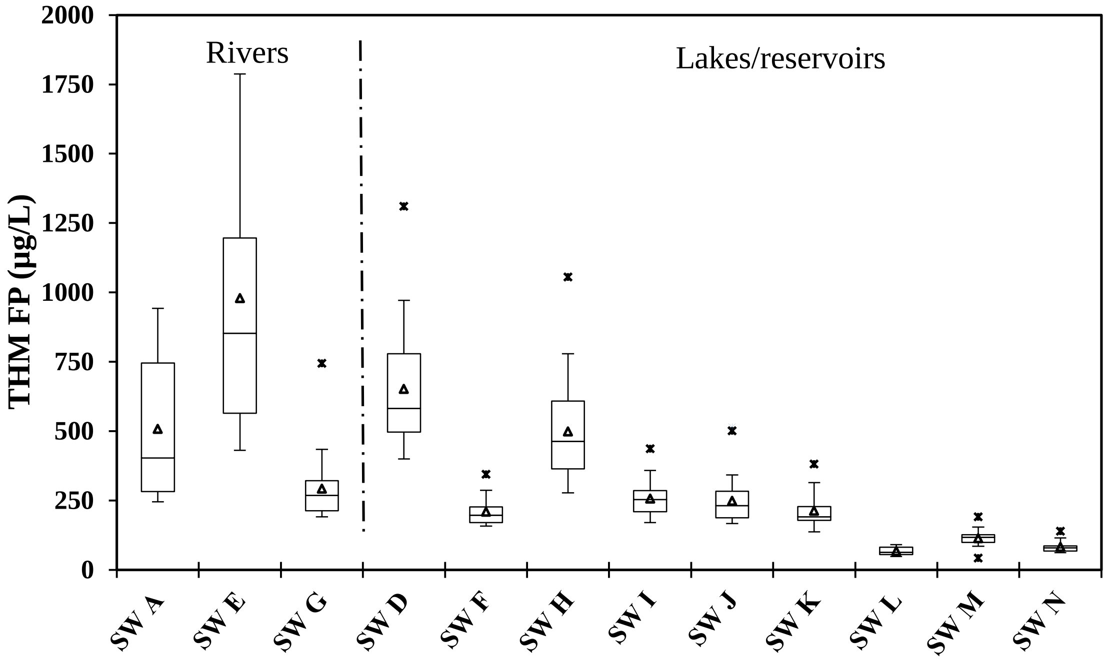


Figure 5.4. THM formation potential of source waters.

SW G showed high NDMA FP but relatively low THM FP, whereas SW D showed moderate NDMA FP but relatively high THM FP. On the other hand, both NDMA FP and THM FP were highest in SW E. Although two rivers, E and G, have exhibited higher NDMA FPs than those of lakes/reservoirs in this work, the same pattern did not exist for THM FPs. These observations indicate that the amount and variability in NDMA precursors are site-specific and the origin and properties of NDMA precursors are different from those of THM precursors (i.e., mainly natural organic matter [NOM] such as humic/fulvic acids). Recent reviews also indicate that nitrosamine precursors are more related to anthropogenic compounds, while THM precursors are related mainly to NOM (e.g., Krasner et al., 2013).

To gain further insight, water samples collected from source waters of nine WTPs during four sampling events in two different seasons (i.e., Jul., Aug., Sep., Nov. 2012) were analyzed with fluorescence excitation-emission matrices and parallel factor analysis (EEM-PARAFAC) (Yang et al., 2014). Three fluorescent components, including two humic-like and one tryptophan-like, were identified for the samples using PARAFAC. Among the three PARAFAC components, the total THM FP was correlated most strongly with humic-like component C2 at the longest emission wavelength, while NDMA FP showed relatively high correlation with the tryptophan-like component C3 (Yang et al., 2014). A strong tryptophan-like fluorescence has been reported for sewage samples (Henderson et al., 2009; Yang et al., 2014), and effluent-impacted source waters are suggested to be of high importance for nitrosamine formations in drinking waters (Krasner et al., 2013).

Linear correlations between water quality parameters (e.g., DOC, $SUVA_{254}$, DON, and etc.) and NDMA FP or THM FP were also examined. The first set of correlations to be discussed here is between the cumulative data set (i.e., all source waters) and NDMA FP. The correlations for individual source waters were also examined (data not shown). THM FP showed a good correlation with DOC (R^2=0.81, **Figure 5.5**), which is consistent with the fact that dissolved organic matter (DOM) is the major precursor of THM in natural waters. In contrast, a weak correlation (R^2=0.11) was observed between NDMA FP and DOC (**Figure 5.6**). Since NDMA formation requires nitrogenous organic compounds reacting with chloramines, the correlation between NDMA FP and DON were examined, but only a weak correlation was found (R^2=0.13, **Figure 5.7**). NDMA FPs are not correlated with THM FPs, suggesting a different nature of their precursors. There was also a poor correlation between NDMA FP and DON/DOC (R^2<0.01, data not shown). This indicates that different types of site-specific precursors in the DON pool play a role in the NDMA formation. NDMA FP showed random or weak correlations with $SUVA_{254}$, boron, and bromide (R^2=0.12, 0.06, and 0.08, respectively, data not shown). **Figure 5.8** shows the correlation between NDMA FP and THM FP with R^2=0.14. This further indicated that the precursors of THM and NDMA are quite different in origins and properties.

Overall, NDMA FP patterns in the 12 source waters during the monitoring period were different from those of THM FP indicating that NDMA and THM do not share common precursors in the sources investigated.

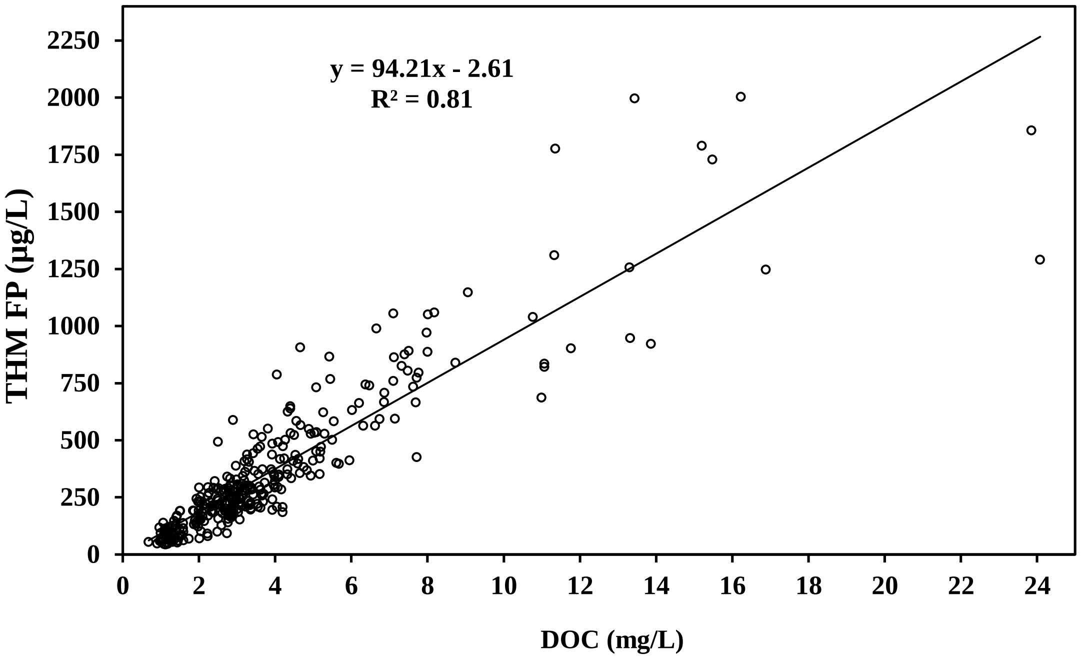


Figure 5.5. Linear correlation between THM FP and DOC (# of data points n=331).

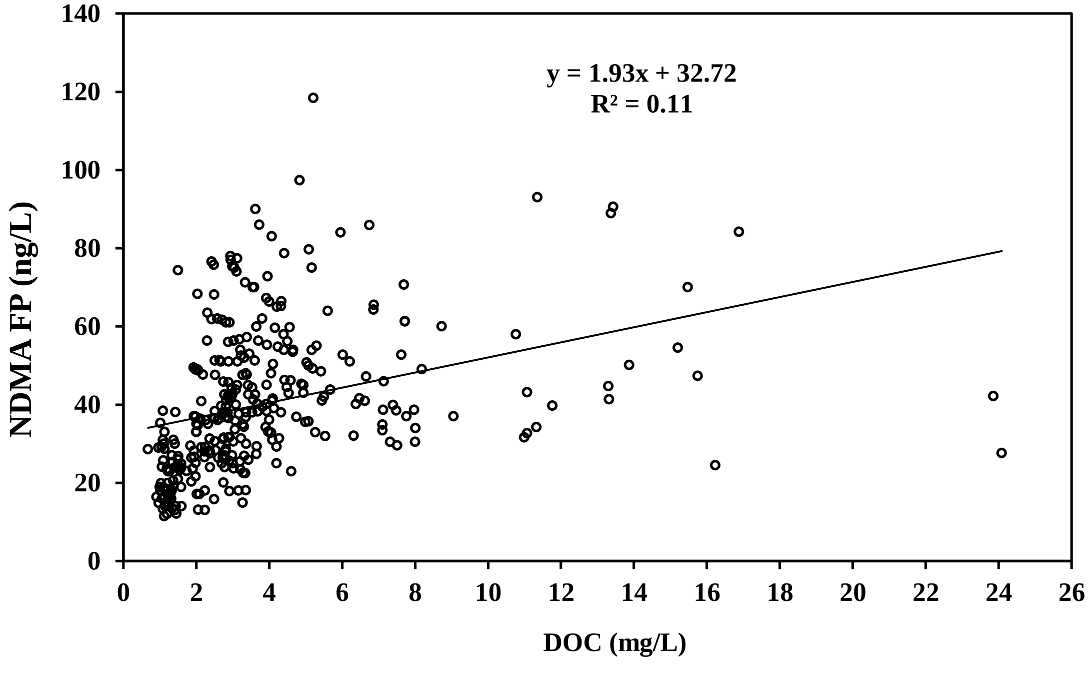


Figure 5.6. Correlation between NDMA FP and DOC (# of data points n=332).

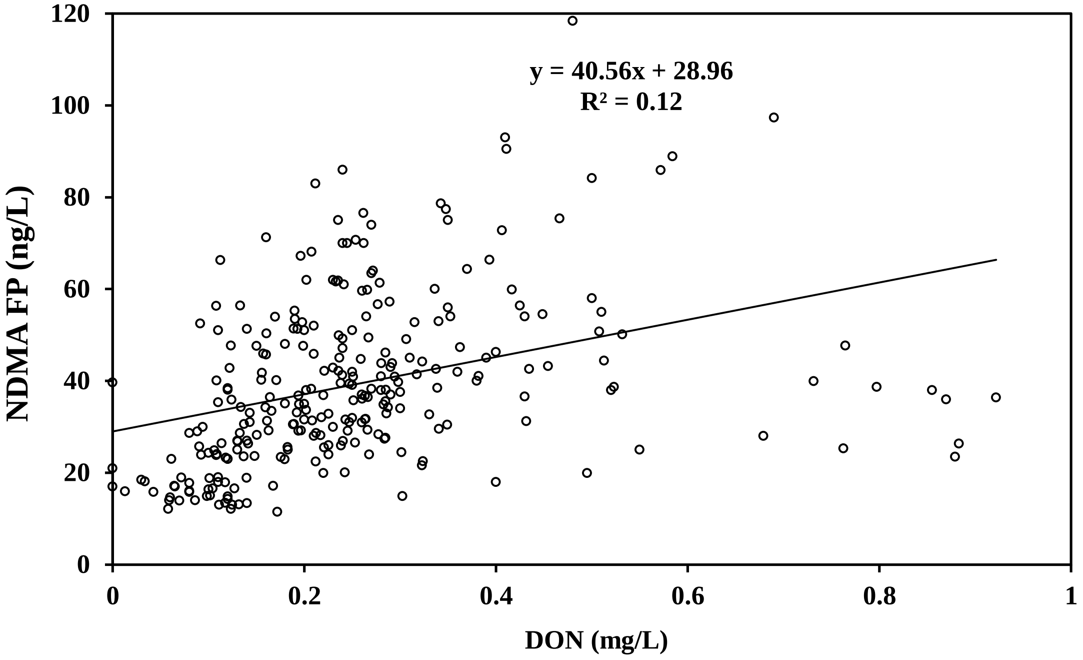


Figure 5.7. Correlation between NDMA FP and DON (# of data points n=289).

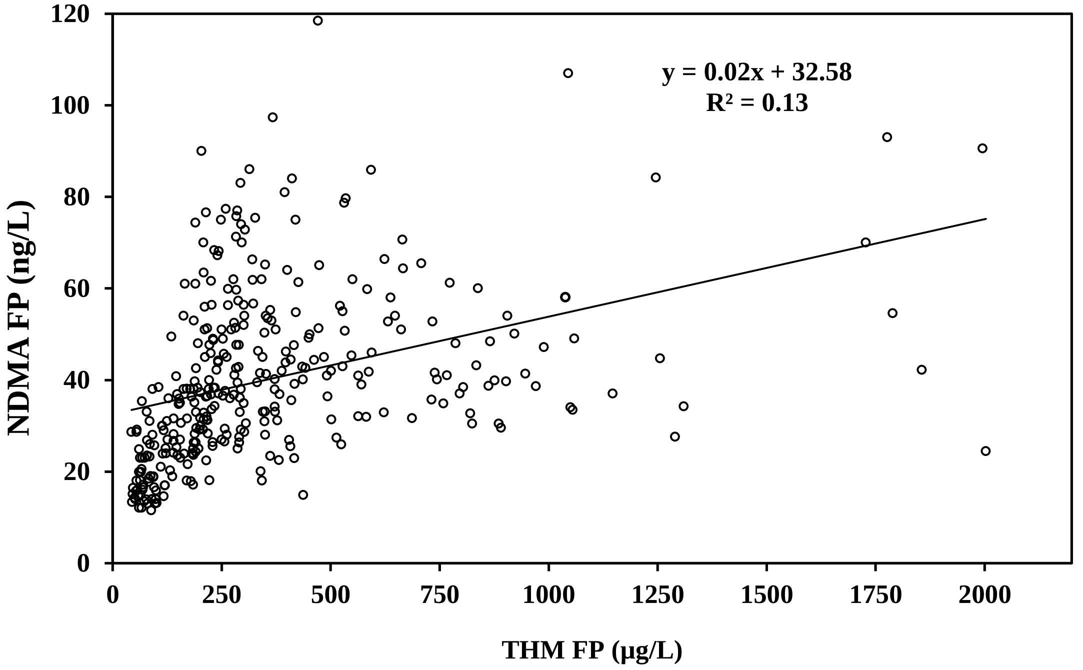


Figure 5.8. Correlation between NDMA FP and THM FP (# of data points n=344).

Multiple linear regressions was employed in order to develop correlations between NDMA FP and water quality parameters (i.e., DOC, $SUVA_{254}$, DON, bromide, sucralose, and THM FP). Fitting equations were obtained using statistical analysis system (SAS) v.9.2 software. The generalized linear selection (GLM) procedure of SAS was applied for parameter selection. The least absolute shrinkage and selection operator (LASSO) was employed for variable selection and determination of coefficients. LASSO is an operator that simultaneously selects the variable and determines the coefficient which is superior to ordinary least square estimates providing interpretable coefficients and avoiding multicolinearity and inflated correlation coefficients. The GLM procedure of SAS was applied to estimate the coefficients of selected variables. LASSO indicated that DOC and log sucralose were significant factors and the other water quality parameters were insignificant. For 32 dataset coefficients that were calculated, the equation was given as follows;

$$\text{NDMA FP} = 3.30\ \text{DOC} + 8.00 \log[\text{sucralose}] + 2.27\ (R^2=0.53)$$ **Equation 5.1**

The result shows that individual correlations of DOC and log sucralose with NDMA FP (R^2=0.38 and 0.22, respectively) may be improved by the multiple linear regressions. This analysis covers only data for Aug 2012, Apr, and Nov 2013 when sucralose samples were collected. This indicates that the multiple linear regressions may provide better correlation coefficients than individual variables for predicting NDMA formation. Although larger data sets will be required to further assess to the ability of predicting NDMA FP with multiple linear regression analysis, the finding of DOC and sucralose emerging as the significant factors in this study provide further support for the anthropogenic nature of NDMA precursors.

Seasonal and Weather Related NDMA FP Patterns

For each source water, monthly measured NDMA FPs were plotted for four different seasons; spring (Mar-May), summer (Jun-Aug), fall (Sep-Nov), and winter (Dec-Feb). **Figure 5.9** shows the seasonal patterns of NDMA FP in all 12 sources. Higher variability in NDMA FP was observed in spring months for most sources, but seasonal mean values, which are denoted with triangles, were relatively consistent regardless of seasons or anthropogenic impacts. In terms of mean values, NDMA FPs of SW E and H were higher in spring and summer, respectively. For SW E, significantly higher seasonal mean value was observed in spring ($p<0.05$). However, for SW H, seasonal mean values were not significantly different ($p>0.05$).

Relatively high variability of NDMA FP at some sources in spring months may be caused by different conditions such as heavy rain events, agricultural activities, or wastewater effluents around watersheds. As for SW E and H, both higher variability and seasonal mean values observed in spring and summer, respectively, suggest that higher amount of NDMA precursors entered these water sources in spring and summer, respectively.

For the purpose of comparison, the seasonal patterns of THM FP were also plotted in **Figure B.2**. The seasonal average of THM FP in SW E increased remarkably in summer months. SW D and H showed moderate levels of THM FP with moderate variability, and changes in their seasonal average values were insignificant. SW F, J, K, L, M, and N showed relatively low and consistent THM FP regardless of the seasons. Although a general analysis of seasonal patterns is presented, a further analysis was conducted to examine the effects of rain and watershed characteristics on the observed temporal patterns in the following sections.

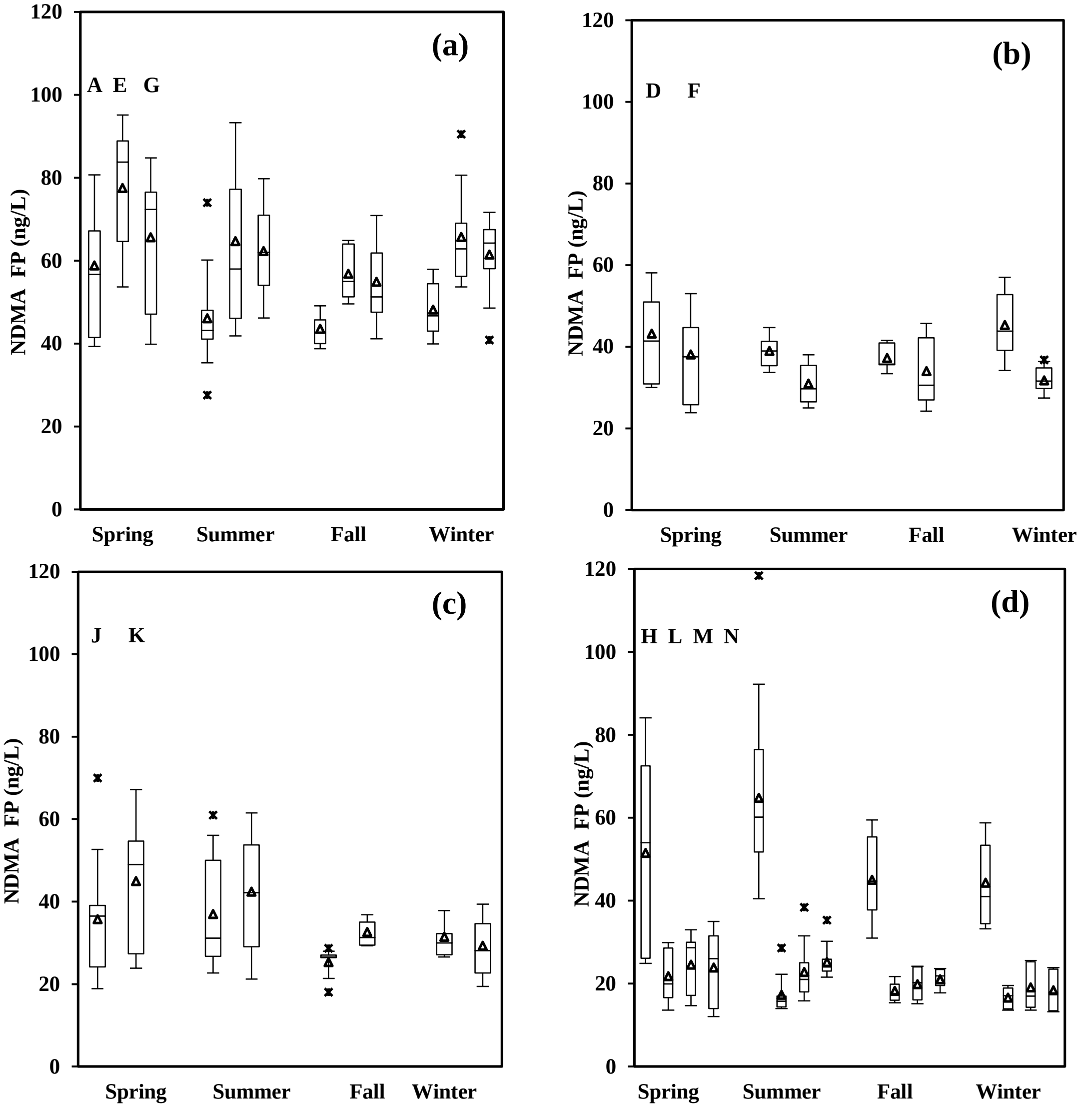


Figure 5.9. Seasonal patterns of NDMA FPs in (a) anthropogenically impacted rivers, (b) anthropogenically impacted lakes/reservoirs, (c) anthropogenically low impacted river and reservoir and (d) limited impacted lakes/reservoirs.

The Impact of Precipitation on NDMA FP

Daily precipitation data for the source water areas near the sampling sites and river flow information were obtained from drinking water treatment plants and USGS stations, respectively, to investigate the impact of rainfall on NDMA FP. While rainfall data were used to examine the impact of rain on rivers and reservoirs, river discharge data were considered for the river systems given the fact that some rivers in this study had upstream dams or impoundments controlling the flow.

The historical regional average precipitation in the project area (1961-1990) was 49.6 inch/year or 0.13 inch/day. During the study period, the cumulative rainfall data were plotted for each site and NDMA FPs were examined for distinctively different rainfall periods: wet (i.e., above the average precipitation of 0.13 inch/day) and dry (i.e., below the average precipitation) periods. An example cumulative rainfall plot showing wet and dry periods belongs to SW L is presented in the **Figure 5.10**. All the others are presented in the **Figures B.3-B.7**. It is noted that most source waters received much more rain than the average between Dec 2012 and Aug 2013. Therefore, two obviously different rain patterns were observed in the study area: regular wet and dry periods for the first half of the study and a long wet period in the second half. The average NDMA FP in most source waters was higher with more variability during the wet (higher rainfall than an average) than dry (lower rainfall than an average) periods suggesting more input of NDMA precursors, while the average values of NDMA FP in SW L, M, and N, the three limited impacted source waters, were lower indicating that precursors in these sources were diluted as a result of rain events (**Figure 5.11a**). SW F showed relatively constant NDMA

FP levels regardless of precipitation. This analysis with more than 20 months of data set indicates that certain types of organic materials carried into source waters or increased discharges from upstream WWTPs during the wet period may account for enhanced NDMA FPs observed at intakes of WTPs. During the wet period, the average values of THM FPs were higher with more variability in the three river systems (SW A, E, and G) and SW D than in the other lakes/reservoirs (**Figure 5.11b**). This was due to additional natural organic matter, a main precursor of THM, brought into the water sources as a result of rain events, which was confirmed by the increasing DOC levels observed during the period. In most lakes and reservoirs, except SW D, however, THM FPs were lower during wet than dry period indicating some dilution effects.

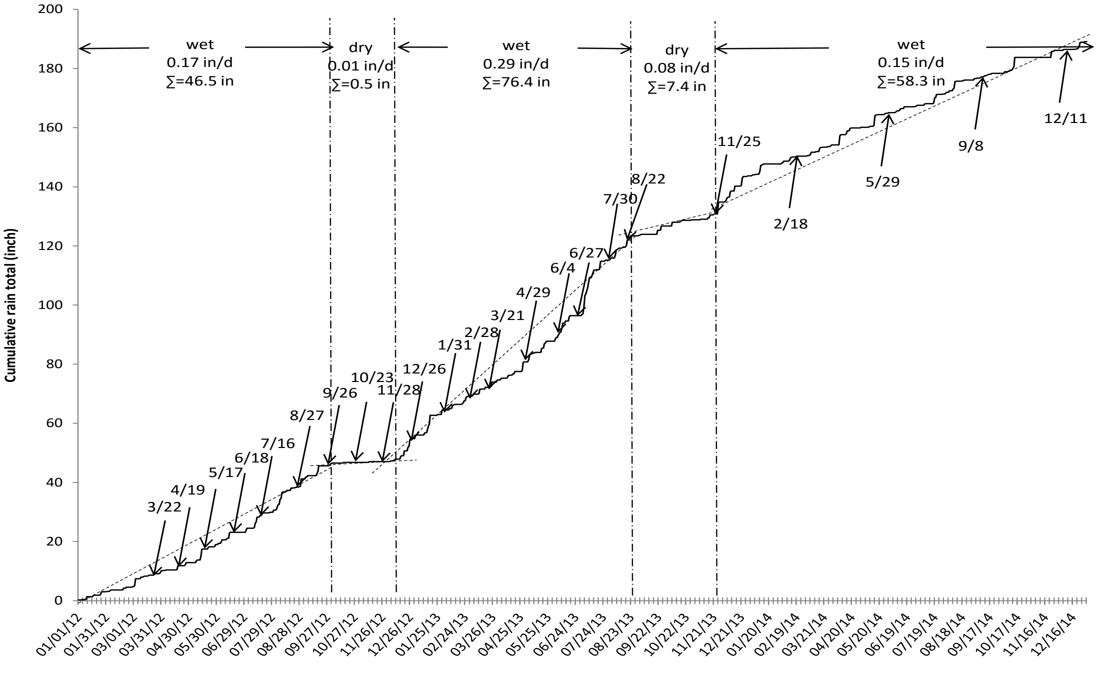
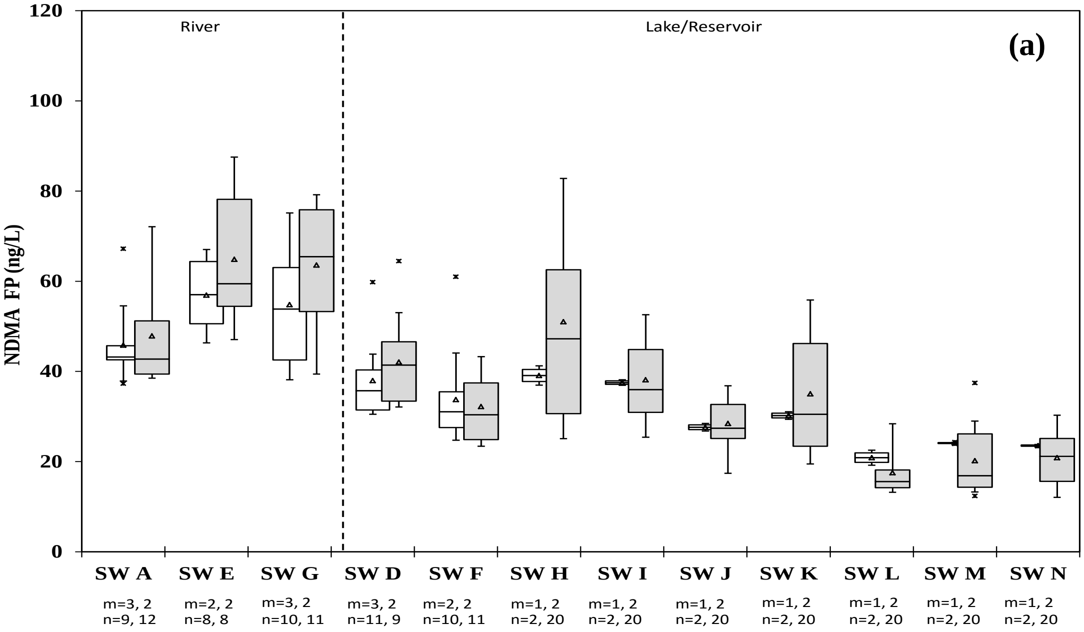


Figure 5.10. An example of the cumulative rainfall plot for SW L showing wet (i.e., having rainfalls above the historical regional average 0.13 inch/day) and dry (i.e., having rainfalls below 0.13 inch/day) rainfall periods.



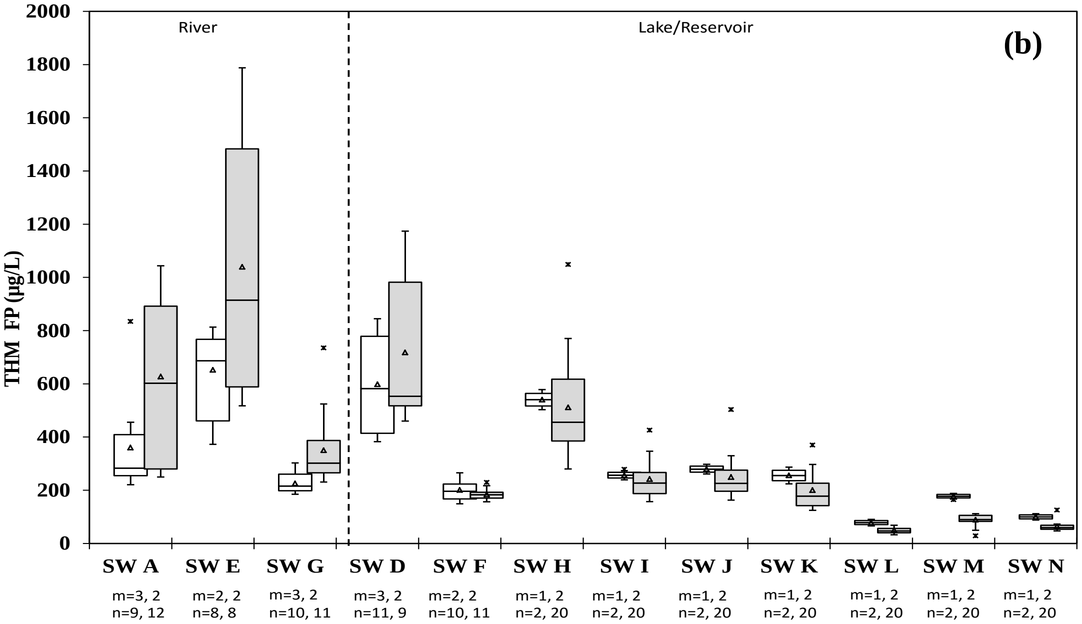


Figure 5.11. (a) NDMA FP and (b) THM FP in dry (white) and wet (gray) periods. m= # of dry and wet periods observed and n= # of samples for each period.

The Effect of Watershed Dynamics on NDMA FP

Especially in river systems, the impact of precipitation depends also on the watershed characteristics such as i) the management of upstream dams, if present, controlling the river flow that may change the effect of organic matter and DBP precursors loads to the downstream waters, and ii) the influence of upstream wastewater discharges that might contribute NDMA precursor concentration levels in source waters. Therefore, the precipitation effects were further analyzed considering the characteristics of selected watersheds. The discharge rates (data obtained from USGS monitoring sites) of river SW G was controlled by upstream dams, while that of SW E (upstream WW impacted source) without any upstream dam was controlled by the local rain events.

In SW G, relatively constant NDMA FP patterns over time were observed (**Figure B.8**). A watershed monitoring study in SW G also revealed that upstream NDMA FPs were higher than those at the intake and their levels decreased right after a dam (a reservoir located on the river) and maintained until the intake. This suggests that a big water body may serve as a buffer zone or an equalization basin for NDMA precursors (**Figure 5.12**).

In SW E (WW impacted river), the river with no upstream dam, the NDMA FP levels varied between 40 and 80 ng/L, which appear to be independent of local rain events or changes in the river discharge. Unlike NDMA FP, however, DOC and THM FP levels increased with elevated discharge rates in SW E (**Figure B.9**).

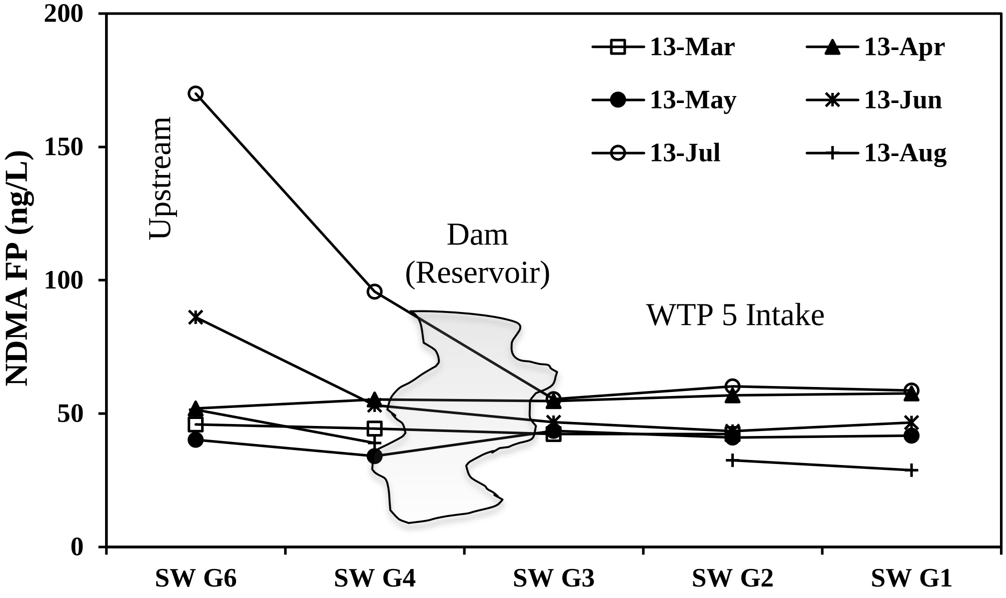


Figure 5.12. NDMA FP at different sampling points of SW G watershed. A reservoir shown on the SW G serves as an equalization basin for NDMA precursor materials.

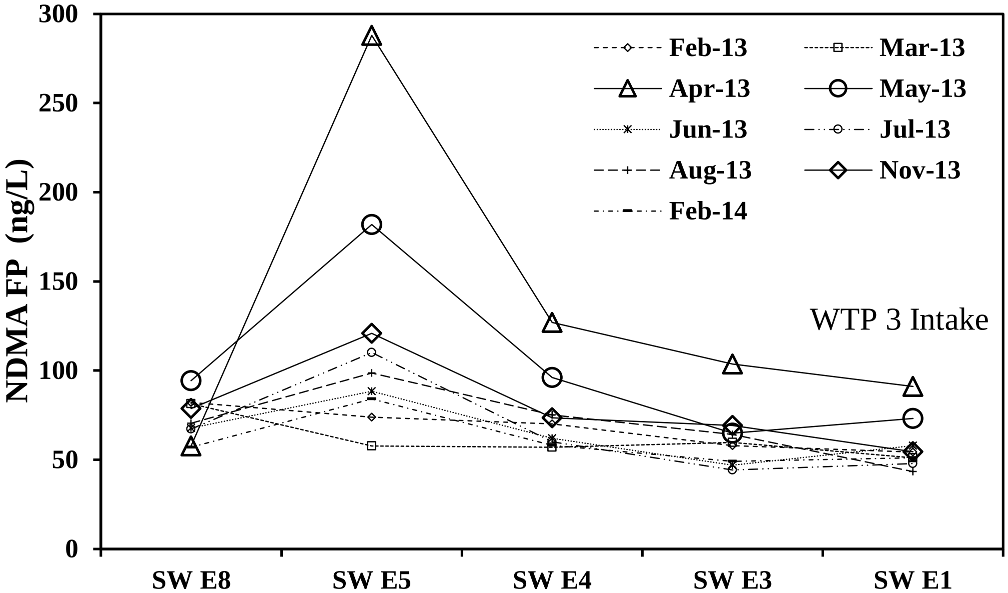


Figure 5.13. NDMA FP at different sampling points of SW E watershed. WWTP effluent discharge influenced SW E5 which is located in the upstream of SW E1 where NDMA FPs were monitored monthly.

A watershed monitoring study conducted on SW E showed that i) upstream wastewater effluent influenced the NDMA PF levels at the intake location of the WTP (**Figure 5.13**), and ii) NDMA FP levels increased as the ratio of WWTP discharge to river discharge increased from 1% to 2%, while the impact of WWTP effluent decreased during the high flow periods due to precipitation. The impact of wastewater effluent was greater when the river discharge rates were lower (**Figure 5.13 and 14**). However, its contribution to the main stream of SW E was diminished with the distance due to dilution.

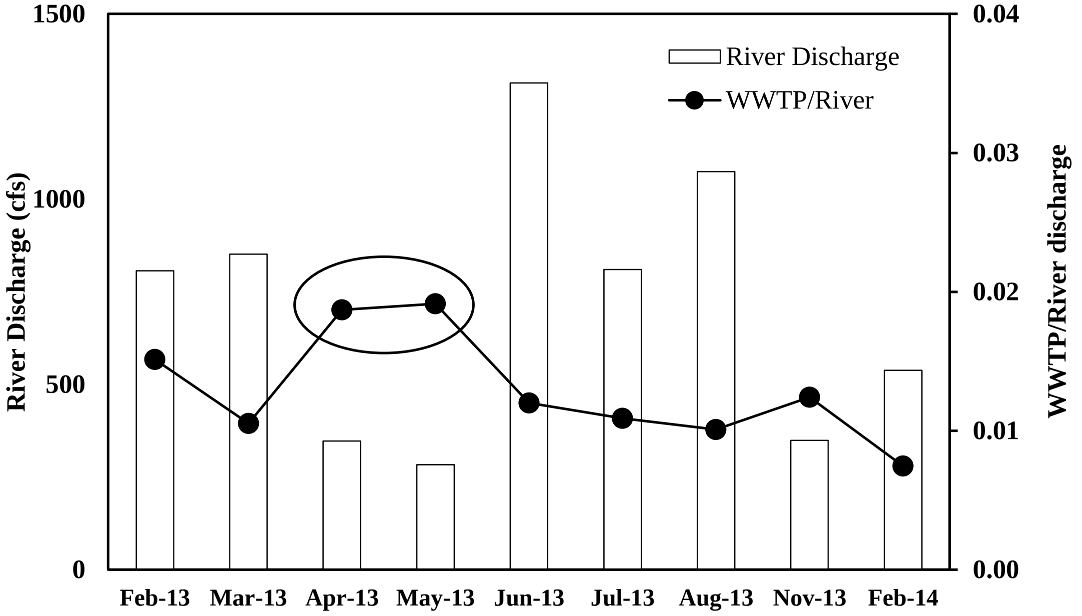


Figure 5.14. WWTP/river discharge ratios at SW E5.

Conclusions

The characteristics of watersheds exerted important influence on the seasonal and weather related patterns of NDMA FP in source waters monitored in this study. In the dam controlled river system (SW G), the NDMA FP levels at sampling locations were controlled by the NDMA levels in the upstream dams independent of the increases in discharge rates due to water releases from the dams prior to or during the heavy rain events or intermittent high NDMA FP levels observed at upstream of dams. The large reservoirs and impoundments on anthropogenically impacted rivers appeared to serve as an equalization basin for NDMA precursors. NDMA FP in the reservoirs remained relatively consistent during the monitoring period and individual rain events around sampling areas did not affect NDMA FP levels, except in three limited impacted reservoirs, NDMA FP levels appeared to be diluted as a result of long term rain events. On the other hand, on a river without an upstream reservoir, the NDMA levels were influenced by an upstream WWTP effluent discharge. In contrast to the NDMA trends, in general, higher DOC and THM precursors in source waters were carried by runoffs or floods due to transport of NOM through the watersheds.

Therefore, understanding watershed characteristics and their influence on NDMA FP is important to determine the seasonal and weather related patterns of NDMA precursors in a source water, thus to develop NDMA control strategies by a water utility. Multiple regression analysis between DOC and log [sucralose] with NDMA FP yielded a better correlation than linear correlations between different water quality parameters and NDMA FP. Despite the empirical nature, if proven to be successful, this type of correlations can be useful to estimate NDMA precursor levels in some source waters.

CHAPTER SIX

THE REMOVAL OF NDMA FP WITH DIFFERENT WATER TREATMENT OPERATIONS

Introduction and Objectives

Water treatment processes (e.g., alum clarification, polymer and PAC applications, membrane treatments, and oxidation) may have different impacts (increase, decrease, or no change) on NDMA FPs. As indicated before, one of the most effective strategies to minimize NDMA formation in the distribution system would be to remove or deactivate NDMA precursors during water treatment before chloramination. Since the future NDMA regulations are expected to be at ng/L levels, many WTPs have a strong interest in understanding the robustness of their processes/operations on the removal/deactivation of NDMA precursors, while complying with the Stage 2 D/DBPR. Therefore, understanding the fate of NDMA and other nitrosamine precursors during drinking water treatment processes under dynamic operational conditions is important to assess the NDMA and nitrosamine formation control during water treatment while complying with other treatment objectives (e.g., regulated DBP control, taste and odor management, iron, manganese control, etc.). NDMA FP removals during the conventional clarification processes have been reported in literature depending on types of source water, different coagulants, applied polymers types, and pre-oxidation (**Table 6.1**). A few studies have shown that NDMA FP changes were negligible with alum (Sacher et al., 2008) and ferric chloride clarifications (Knight et al., 2012) at full scale WTPs. However, other studies observed an increase in the NDMA FP after conventional clarification (i.e., coagulation, flocculation and sedimentation) compared to raw water (Krasner et al., 2008; Krasner et al., 2012; Sacher et al., 2008; Mitch et al., 2009). Such increased NDMA FP was attributed to the usage of flocculation aid polymers during conventional clarification processes. It has been reported that some polymers (e.g., aminomethylated polyacrylamide, poly(epichlorohydrin dimethylamine) and poly (diallyldimethylammonium chloride)) used commonly for water treatment could increase NDMA FP levels (Kohut and Andrews, 2003; Wilczak et al., 2003; Mitch and Sedlak, 2004; Najm et al., 2004; Park et al., 2007; Park et al., 2009). PAC application led to increases in the NDMA FP removals from surface waters and wastewater effected source waters (Sacher et al., 2008; Hanigan et al., 2012; Beita-sandi et al., 2016). Furthermore, it has been reported that microfiltration and ultrafiltration membranes were not effective for the removal of NDMA precursors (Pehlivanoglu-Mantas and Sedlak, 2008; Krauss et al., 2010), while nanofiltration (NF) and reverse osmosis (RO) membranes achieved 76-98% (Miyashita et al. 2009) and >98% (Schmidt et al. 2008; Krauss et al., 2010) NDMA FP removals, respectively. It has also been known that the bulk portion of NDMA precursors consists of small molecular weight compounds and can pass through 3000 Da ultra-filters (Mitch and Sedlak, 2004; Pehlivanoglu-Mantas and Sedlak, 2008).

Table 6.1. The effect of conventional clarification processes on NDMA FP removal – Literature summary.

	Raw Water	Coagulant	Coagulant Dose (mg/L)	Polymer	Pre-oxidation	NDMA FP removal (%)	Reference	Notes
Full scale WTPs	Wastewater Impacted River	Alum	N/A[a]	Cationic	Cl_2	Increased[b]	Krasner et al., 2008	Polymer contributes to NDMA FP
	River	$FeCl_3$	17-42	None	Cl_2 (1.9-2.4 mg/L)	19-87	Sacher et al., 2008	NDMA FP removal was attributed to pre-oxidation with chlorine
	Ground Water	Alum	15	Cationic	Cl_2[c]	19		
	River & Reservoir	Alum	40-60	None	Cl_2	55		
	River (90%) & Ground Water (10%)	Alum	N/A	None	ClO_2 (0.8 mg/L)	High[d]		NDMA removal was attributed to pre-oxidation with chlorine dioxide
	Lake	$FeCl_3$	N/A	Coagulant aid	None	-900[e]		NDMA FP was attributed to the coagulant aid (not specified)
	River & Lake (5 WTPs)	N/A	N/A	Mostly PolyDADMAC	N/A	-82 to 18	Mitch et al., 2009	For most of the plants, NDMA levels were higher after coagulation due to polymer effect
	Wastewater or Algae Impacted Waters (seven WTPs)	$FeCl_3$	~33	Cationic	N/A	-43 to -82	Krasner et al., 2012	Cationic polymers contributed to NDMA FP; coagulation alone at one plant removed NDMA FP -18 to 18 %.
				None (one WTP)	N/A	-18 to 18		
Bench scale tests	Wastewater Impacted River	$FeCl_3$ and $AlCl_3$	0-10	None	None	<10 %	Sacher et al., 2008	NDMA FP removal was negligible
	River	$FeCl_3$	30	None	None	No change	Knight et al., 2012	No reduction in NDMAFP
		Alum						

[a] N/A: Not Available, [b] NDMA FP was higher after coagulation/flocculation as compared to the influent water,
[c] after sedimentation before filtration, [d] quantitative information was not available, [e] negative removal indicates the increase in the NDMA FP.

In addition, Chen and Valentine. (2008) showed that an appreciable amount of NDMA precursor was deactivated with only chlorine (Cl_2) addition for a short contact time (e.g., 10-20 minutes). Shah et al. (2012) reported that chlorination with its Ct (oxidant concentration × contact time) value of 37 mg*min/L reduced the NDMA formation up to 80% during subsequent chloramination, but further increases in Ct did not lead to additional reduction. Unlike chlorination, however, chlorine dioxide (ClO_2) oxidation may have both positive and negative impacts on formation of NDMA during subsequent chloramination (Lee et al., 2007; Sacher et al., 2008; Shah et al., 2012; Selbes et al., 2014).

Although different treatment processes have been examined, the robustness and variability of NDMA precursor control under dynamic operation of full-scale water treatment plants have not been investigated in long term monitoring studies. Therefore, the main objectives of this task of the study were i) to examine the removal efficiency of NDMA precursors measured by FP tests at full-scale WTPs for an extended monitoring period (18 months), ii) to assess the NDMA FP by different treatment processes (e.g., alum clarification, PAC adsorption, DAF, membrane filtration, pre-oxidation and post-oxidation across WTPs, and iii) to evaluate NDMA occurrence levels in distribution systems. In addition, the change in the FPs of six other nitrosamine species (i.e., NPYR, NDBA, NMEA, NDEA, NPIP, and NDPA), and regulated THM were also monitored for comparison purposes. A long term monitoring plan in this study also captured the impacts of weather events such as different seasons and dry/wet periods on the removal efficiencies.

Sample Collection and Analysis

In order to explore the objectives, samples were collected on a monthly basis from February 2012-August 2013, and then on a quarterly basis until February 2014 from nine WTPs. Specifically, for each WTP, water samples were collected from the influent (i.e., raw water), clarifier or DAF effluents (only for WTP 9), after post-oxidation with Cl_2 and/or ClO_2 (i.e., POE), and the longest point in the distribution system (**Figure C.1**). The NDMA FP removal efficiencies for conventional clarification and post-oxidation were calculated using following equations;

$$\text{Conventional removal \%} = [(C_{raw} - C_{eff})/C_{raw}] \times 100 \qquad \textbf{Equation 6.1}$$

$$\text{Post oxidation removal \%} = [(C_{eff} - C_{oxi})/C_{eff}] \times 100 \qquad \textbf{Equation 6.2}$$

where, C_{raw}=NDMA FP (ng/L) in raw water, C_{eff}=NDMA FP (ng/L) in treated water (i.e., clarifier effluent, before filters and any oxidant addition), C_{oxi}=NDMA FP (ng/L) after post-oxidation (i.e., at POE).

NDMA and THMs were extracted and analyzed using GC/MS/MS and GC/ECD, respectively. Chemical standards, analytical methods used for NDMA, THMs, other water quality measurements and jar tests experimental procedures are explained in Chapter Four.

Since NDMA FP has been predominant among nitrosamines FPs observed in raw waters of the monitored WTPs, this chapter focused mainly on the removal of NDMA FP and the occurrence of NDMA. However, the FP values of other nitrosamines measured across WTPs for the first nine-month monitoring are also provided in **Table C.1**. In addition, THM FPs and selected water quality parameters (e.g., DOC, UV_{254}, $SUVA_{254}$ [UV_{254}/DOC], DON, NO_3^-, NO_2^-, Br^-, and NH_3) were also monitored at the plans influents and across treatment process trains, and some parameters were compared with the NDMA FP removal trends.

Typical Operational Conditions of Water Treatment Plants

Table 6.2 provides a summary of process configurations of the WTPs monitored in this study. All WTPs used alum for coagulation and applied alum doses depended on DOC and/or turbidity levels in the influents. WTPs 4 and 5 applied 2-3 mg/L of PAC continuously, while WTPs 2 and 3 used 1-10 mg/L of PAC occasionally to control taste and odor problems. WTPs 1, 4, 5, and 8 applied different pre-oxidation strategies including Cl_2 and/or ClO_2, and NH_2Cl before conventional clarification, and WTPs 1, 2, 3, 4, and 5 applied three different types of polyacrylamide polymers (i.e., Optimer Nalco Pulv 8110, Nalco 8170, and Sedifloc 400C) into their flocculation basins and/or rapid mixing units. A small RO system at WTP 1 was operated occasionally as needed to supply water to a nearby power plant. WTP 7 used a MF unit in addition to conventional clarification and a DAF system was used at WTP 9 instead of a sedimentation process. WTPs 6 and 7 utilized Cl_2 as a final disinfectant to maintain residual in the distribution system, while the other seven WTPs used Cl_2 (with/without ClO_2) for the post-oxidation prior to NH_3 addition to form chloramines. The typical average water ages in distribution systems estimated by the utilities ranged from 1 day to 14 days. The occurrences of NDMA was monitored at the longest detention time location in each distribution system.

Although not listed on **Table 6.2,** WTPs also use various chemicals including alum for coagulation, lime or caustic for pH adjustment, polyacrylamide polymers as flocculation aid, phosphate based corrosion inhibitor, and fluoride to prevent tooth decay. More detailed information about these treatment plants was also presented in **Appendix A**.

Water Quality Parameters of Influent Water and Process Configurations of WTPs

Nine conventional WTPs located in the southeastern US using twelve different surface waters were selected for this study. Measured NDMA FP, THM FP, and selected water quality parameters of WTP influent waters are listed in **Table 6.3** showing a wide range of characteristics. Dissolved organic carbon (DOC), specific ultraviolet absorbance at 254 nm ($SUVA_{254}$), dissolved organic nitrogen (DON), bromide, and boron values were 0.7-16.2 mg/L, 0.6-5.7 L/mg-m, <MRL-0.62 mg/L, <MRL-487 µg/L, and <MRL-76 µg/L, respectively. NDMA FPs ranged from 12 to 98 ng/L, while THM FPs were between 45 and 2002 µg/L with a relatively high variability. The occurrence levels of NDMA and THMs in all plant influents were always below the MRLs.

Table 6.2. Process configurations of WTPs.

WTPs	Source Waters	Pre-oxidants and/or PAC	Treatment Type	Polymer Addition	Disinfection Strategy	~ Longest Water Age in the Distribution Systems
1	[a]SW A-River [b]SW B-Reservoir	None Cl_2	Conv. T. & RO	Polymer Nalco 8110 (0.03 ppm)	*Cl_2 before filters, *Cl_2 after filters before Clearwells, *NH_3 addition to form NH_2Cl before POE	~1-2 days
2	SW A- River [c]SW C-Reservoir	None PAC	Conv. T.	Polymer Nalco 8110 (0.02 ppm)	*Cl_2 before filters, *Cl_2 after filters before Clearwells, *NH_3 addition to form NH_2Cl before POE	~5 days
3	SW D-Reservoir SW E-River	None PAC	Conv. T.	Polymer Nalco 8170 (0.03 ppm)	*Cl_2 and/or ClO_2 before and after filters, *Cl_2 and NH_3 addition to form NH_2Cl before POE	~14 days
4	SW F-Lake	ClO_2 & Cl_2 PAC	Conv. T.	Polymer Sedifloc 400 C (0.25 ppm)	*Cl_2 before filters, *Cl_2 and NH_3 addition to form Cl_2 after filters, before Clearwells *NH_3 addition to form NH_2Cl before POE	~4 days
5	SW G-River	ClO_2 & Cl_2 PAC	Conv. T.	Polymer Sedifloc 400 C (0.25 ppm)	*Cl_2 before filters, *Cl_2 and NH_3 addition to form NH_2Cl before Clearwells	~5 days
6	SW J-River	None	Conv. T.	None	*Cl_2 before filters, *Cl_2 after filters before Clearwells	~7 days
7	SW K-Reservoir	None	Conv. T. + MF	None	*Cl_2 after MF before Clearwells	
8	SW L-Lake	Cl_2 & NH_3	Conv. T.	None	*NH_2Cl after filters before Clearwells	~10 days
9	SW M-Reservoir SW N-Reservoir	None	Conv. T. + DAF	None	*Cl_2 before filters, *Cl_2 after filters before Clearwells *NH_3 addition to form NH_2Cl before POE	~5 days

SW: Source Water, MF=Microfiltration, DAF=Dissolved Air Flotation, PAC=Powdered Activated Carbon, Conv. T.=Conventional Treatment, POE=Point of entry. Entry. [a] About 300 mile long river and a common source for the SW B and SW C, .[b]SW A is pumped into the reservoir (SW B) and the effluent of reservoir serves as a raw water for the WTP1. [b]SW A flows into a reservoir (SW C) after traveling through a 18-mile channel, and the effluent of reservoir serves as a raw water for WTP2.

Table 6.3. Selected water quality parameters in WTP influents.

WTP	Treatment Type	*DOC (mg/L)	*SUVA_{254} (L/mg-m)	*DON (mg/L)	*Bromide (µg/L)	*Boron (µg/L)	NDMA FP (ng/L)	THM FP (µg/L)
1	Conventional	2.8-16.2	2.1-4.4	0.12-0.32	36-230	N/M	25-73	192-2002
2	Conventional	3.0-13.3	2.0-4.7	0.16-0.47	38-242	16-27	29-75	219-1232
3	Conventional	3.9-15.2	2.3-5.7	0.19-0.47	74-487	38-76	31-73	349-1789
4	Conventional	1.4-4.6	1.2-3.2	0.12-0.52	13-52	11-30	23-61	140-306
5	Conventional	2.2-4.2	1.6-3.8	<MRL-0.38	63-316	17-47	26-98	175-461
6	Conventional	1.5-4.3	1.0-4.9	<MRL-0.43	9-46	<MRL-13	17-74	132-502
7	Conventional + MF	1.5-3.4	1.3-3.5	<MRL-0.62	14-52	<MRL-20	18-35	88-321
8	Conventional	0.7-2.0	0.6-1.8	0.10-0.49	9-52	<MRL-9	12-29	45-94
9	Conventional + DAF	0.9-2.2	1.1-3.3	<MRL-0.33	<MRL-14	<MRL-6	12-34	53-123

N/M: not measured, MRL: Minimum reporting level, MF: Microfiltration, DAF: Dissolved Air Flotation.
* Measured or determined for filtered samples with pre-washed 0.2 µm membrane filters.

Results and Discussions

Overall NDMA FP Removals at WTPs

WTPs 6 and 7 are chlorinated plants, while the other plants use chloramines for disinfection of finished water. Due to different source waters and different degrees of anthropogenic impacts, the NDMA FP levels monitored in the influent waters of nine WTPs showed a wide range of values (**Table 6.3**). Nevertheless, after conventional water treatment processes, the overall NDMA FP removal efficiencies calculated by taking the difference between NDAM FPs in the influent and POE of WTPs were relatively consistent (40-59%) except for WTP 8 that had an average of 10% (**Figure 6.1**). All WTPs but WTP 8 applied Cl_2 and/or ClO_2 to obtain Ct credits prior to NH_3 addition. WTP 8 added NH_3 right after Cl_2 addition in the beginning of treatment train (rapid mix) to form chloramines. Therefore the absence of Cl_2 and/or ClO_2 contract likely resulted in very low NDMA FP removals at WTP 8.It is noted that WTPs 4 and 5 used polyacrylamide polymers (Sedifloc

400 C) during alum clarification and that polymer-derived NDMA precursors substantially contributed to the influent NDMA FP levels, but the calculated removal efficiencies from influent to the POE were comparable to those of other conventional WTPs.

The presented results indicate that removal efficiencies (NDMA FP) were closely related to operation conditions rather than NDMA FP levels in the influent waters. The impacts of alum clarification, application of polymers, PAC and oxidants (ClO_2 and/or Cl_2) are discussed in the following sections.

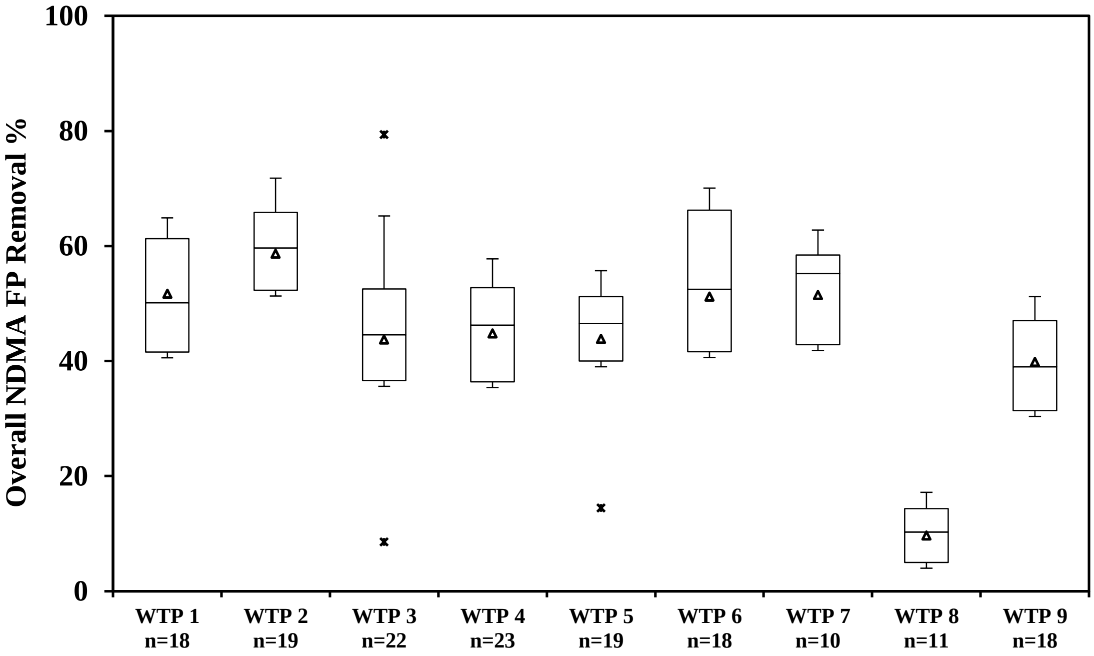


Figure 6.1. Overall NDMA FP removals at WTPs. n denotes # of data.

Impact of Polymers on NDMA FP

Some amine based polymers (e.g., aminomethylated polyacrylamide [Mannich polymer], polyamine and polyDADMAC) used for water treatment can exhibit appreciable levels of NDMA FPs (Kohut and Andrews, 2003; Wilczak et al., 2003; Mitch and Sedlak, 2004; Najm et al., 2004; Park et al., 2007; Park et al., 2009). Park et al. (2009) tested the NDMA FPs of the polymers and reported the order of Mannich >> polyamine ~ polyDADMAC > cationic polyacrylamide.

Five WTPs surveyed in this study applied three different polyacrylamide polymers, Optimer Nalco Pulv 8110, Nalco 8170, and Sedifloc 400C as flocculation aids. NDMA FP tests were conducted with these polymers i) to determine the maximum contribution of polymer-derived NDMA precursors at typical application doses in DDW, ii) to mimic the contribution of these polymers as potential sources of NDMA precursors in natural waters, and iii) to evaluate the removal of polymer-derived NDMA precursors during alum clarification.

NDMA FP in DDW was only 6 ng/L from Optimer Nalco Pulv 8110 used at WTP 1 and WTP 2, while Nalco 8170 used at WTP 3 exhibited NDMA FP below the MRL at typical application doses (i.e., 0.02 mg/L for both polymers) (**Table 6.4**). On the other hand, NDMA FP from Sedifloc 400C used at WTP 4 and WTP 5 was relatively high (~45 ng/L) at typical doses (0.2 mg/L), which was comparable to the NDMA FP levels in the raw waters of those plants. To examine the contribution of polymers to NDMA precursor levels in raw waters, and the removal of NDMA FP (source water precursors + polymer-derived precursors) during coagulation/flocculation, jar test experiments were conducted (polymer dose ~0.2 mg/L, and pH ~6) for the two high NDMA producing polymers (Nalco 8110 and Sedifloc 400C) with three background waters (i.e., DDW, SW A and SW D) collected in Nov 2013, and using 0, 10, and 40 mg/L of alum doses.

Table 6.4. NDMA FP from polymers in DDW.

WTP	Polymer	Application Point	Dose (mg/L)	NDMA FP[b] (ng/L)
1 & 2	Nalco 8110	Flocculation basin	0.01	<MRL
			0.02 [a]	6
			0.05	11
			0.1	27
3	Nalco 8170	Flocculation basin	0.01	<MRL
			0.02 [a]	<MRL
			0.05	<MRL
			0.1	<MRL
4 & 5	Sedifloc 400 C	Rapid mix	0.1	24
			0.2 [a]	45
			0.5	118
			1.0	284

MRL=Minimum reporting level.

[a] Typical application dose at the plants.

[b] Experimental conditions: Oxidant dose=100 mg/L $NHCl_2$, Cl_2:N=4:1, Contact time=5 days, pH~7.8.

During jar test experiments, NDMA FP, THM FP, DOC, DON, $SUVA_{254}$, and turbidity were measured. Two raw waters, SW A and SW D, showed similar NDMA FP values (34 and 37 ng/L, respectively) although their DOC, $SUVA_{254}$ and THM FP values were different (**Table C.2**). In all background waters (i.e., DDW, SW D, and SW A), 0.2 mg/L polymer (either Nalco 8110 or Sedifloc 400C) increased NDMA FPs (**Figure 6.2**). The increases of NDMA FP in DDW was about 47 ng/L in the presence of both polymers (**Figure 6.2a**), whereas NDMA FP increases were only ~13 ng/L and ~10 ng/L for Nalco 8110 in SW A and SW D, respectively, and ~20 ng/L and ~10 ng/L for Sedifloc 400C, respectively (**Figure 6.2b**).

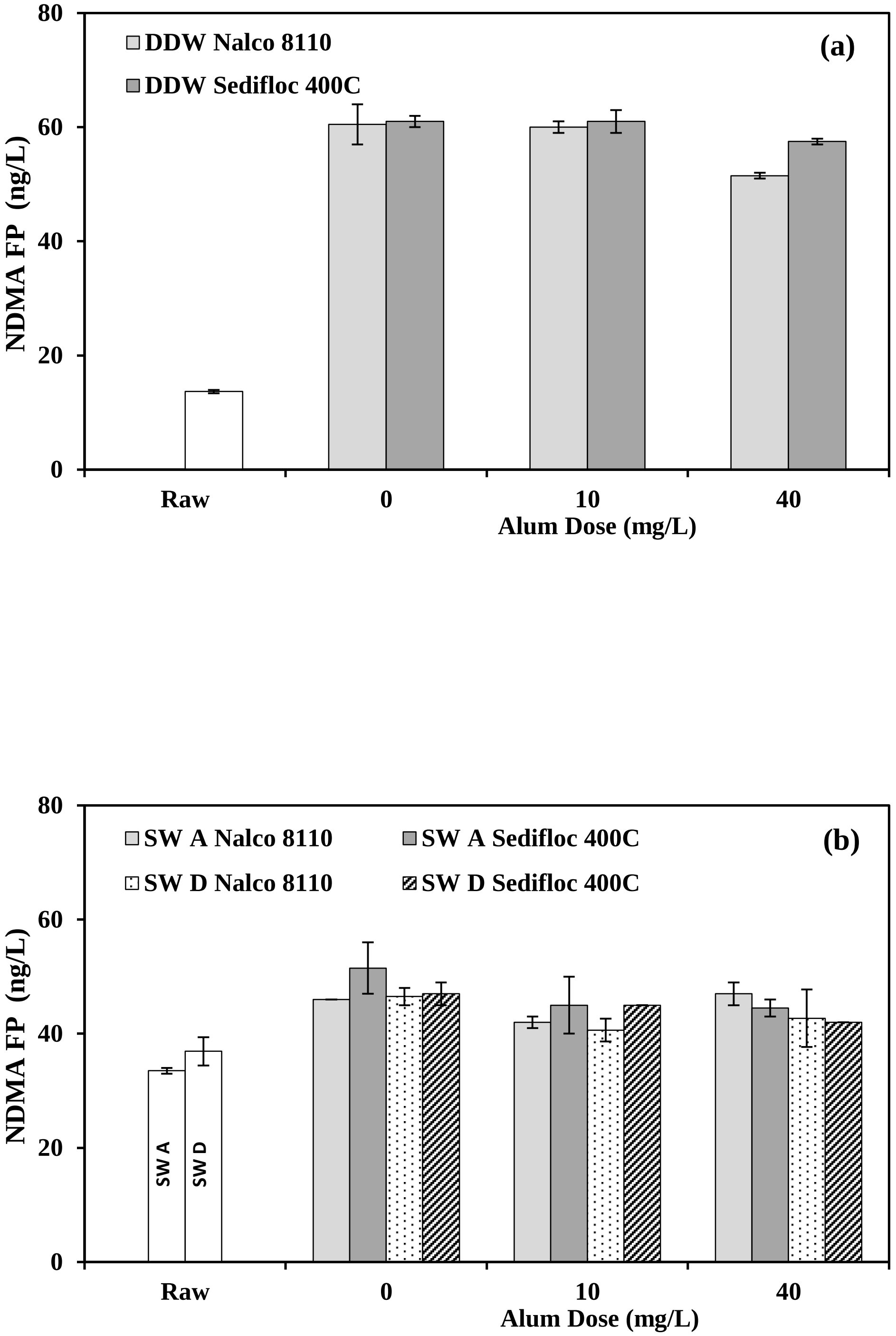


Figure 6.2. Changes of NDMA FP levels during jar tests with (a) DDW and (b) natural waters (SW A and D) in the presence of polymers. Alum doses=0, 10, 40 mg/L (pH~6). Oxidant dose for NDMA FP tests=100 mg/L $NHCl_2$ (Cl_2:N=4:1) and contact time=5 days (pH~7.8). Error bars represent data range for duplicate samples.

It appears that background constituents in natural water may react with polymer-derived precursors either with or without the presence of alum, and as a result the overall NDMA FP significantly decreased compared to the results from DDW. With an increasing alum dose in DDW and natural water samples (SW A and D), NDMA FP changes as a result of coagulation and flocculation were not significant. Almost consistent NDMA FP levels were observed from the jar test experiments with increasing alum doses indicating that polymer-derived precursors are not removed by alum coagulation. Therefore, increases in NDMA FPs of source waters as a result of polymer addition are mainly attributed to the polymer residual that did not react with the background components in natural waters tested.

The Effects of Alum Clarification on NDMA FP Removals

To evaluate the impact of only alum clarification on the removal of NDMA FP, accumulated data obtained from six WTPs for the months when neither pre-oxidant or PAC was applied were investigated and the results were plotted in **Figure 6.3**. Although polymers were used at WTPs 1, 2, and 3, their contributions to the NDMA FPs during water treatment processes are assumed to be negligible at their typical application doses based on the result from the jar test experiments (**Table 6.4 and Figure 6.2b**).

More alum (average 50 mg/L) was used at WTP 2 than at WTP 1 (average 36 mg/L) although both plants received water from the same river. Raw water from the river stayed in two different reservoirs for different detention times before entering the WTPs. Therefore, water quality characteristics of the influents of WTPs 1 and 2 were very similar except turbidity (**Table 6.3**). Because of higher turbidity in the influents of WTP 2 than

WTP 1, however, more doses of alum were applied at WTP 2. An average NDMA FP removal efficiency by alum was 30% at WTP 2, which was higher than that (17%) of WTP 1 (**Figure 6.3**). An 18-mile canal between two reservoirs may change the reactivity of NDMA precursors and the turbidity due to possible inputs of substances from the canal banks and lagoon discharges to the canal.

Average NDMA FP removals at WTPs 3, 6, 7, and 9 using different source waters ranged from 12% to 27%, while THM FP removals ranged from 29% to 64% (**Figure 6.3**). Higher NDMA FP removals by alum were observed at WTPs 2 and 6 than at WTPs 1, 3, 7, and 9. Additional jar test experiments showed that the removal efficiencies by alum clarification process were independent of different water types or applied alum doses (**Figure C.2**). The removal of NDMA FP (average 12%) at WTP 9 with the DAF unit was comparable to those at WTPs 3 (average 13%) and 7 (average 14%) with conventional sedimentation units (**Figure 6.3**), suggesting no advantage/disadvantage of DAF for NDMA FP removals over sedimentation.

Higher THM FP removals by alum observed at WTPs 1, 2, and 3 are attributed to higher DOC and $SUVA_{254}$ in influent waters (**Figure 6.3** and **Table 6.3**). Average DOC removals ranged from 18 to 51% (**Figure C.3**), whereas DON removals were from 4 to 29% with more variability (**Figure C.4**). Overall, the results indicate that the removal of NDMA precursors by alum clarification is variable and relatively low (<20 %) compared to THM FP removals supporting that the nature of NDMA precursors is different from that of THM precursors which are closely associated with humic like substances (Krasner et al., 2008; Uzun et al., 2015).

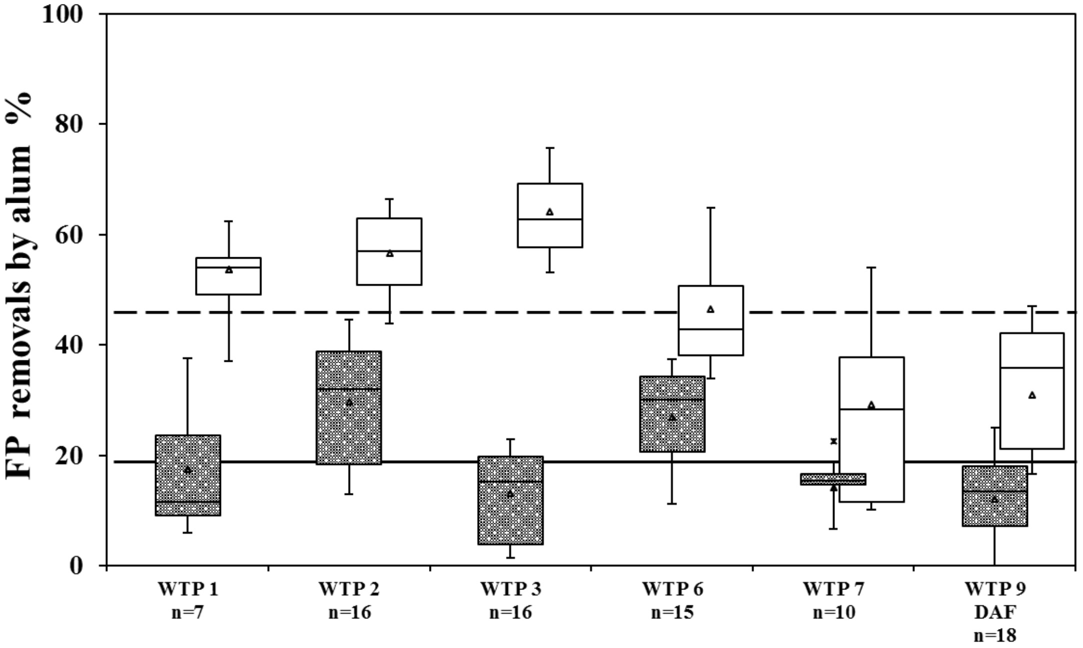


Figure. 6.3. NDMA FP (grey) and THM FP (white) removals achieved by alum clarification. Solid line and dashed line indicate average removals of NDMA FP (19%) and THM FP (45%), respectively. n denotes # of data.

The Effects of Seasonal and Weather-Related Changes on NDMA FP Removal

Seasonal variations in natural and anthropogenic influences on source waters may affect NDMA precursors present in influents and consequently the treatability of WTPs. To investigate seasonal changes of NDMA removal efficiencies by alum clarification, the results monitored for two years at no pre-oxidant applied WTPs (i.e., 1, 2, 3, 6, 7, and 9) were plotted in four different seasons, spring (March-May), summer (June-August), fall (September-November), and winter (December-February) (**Figure 6.4**). However, no apparent change was observed in seasonal NDMA FP removal efficiencies at these six WTPs. Seasonal average values for the NDMA FP removals at each WTP were relatively constant.

On the other hand, seasonal THM FP removals at some WTPs showed somewhat different patterns from NDMA FP removals, but the trends were site-specific (**Figure C.5**). For instance, higher THM FP removals were observed at WTP 2 in spring, at WTP 6 in winter, at WTP 7 in summer and winter, and at WTP 9 in fall. As indicated in Chapter Five, rather than seasonal effects, local weather events (e.g., major rain events, extended wet and dry periods, etc.) directly affected raw water quality including THM FP levels.

Cumulative rainfall data around selected WTPs, including, high (i.e., above the historical regional average 0.13 inch/day) and low (i.e., below the average) rainfall periods were determined, and NDMA FP removal efficiencies in high and low periods were plotted in **Figure 6.5.** However, differences in the average NDMA FP removal efficiencies between high and low periods at each WTP were not statistically significant ($p>0.05$). The average NDMA FP in the source waters of WTPs 1, 2, 3, 6, and 7 was slightly higher and exhibited more variability during high rainfall periods, while an opposite trend was observed in the source waters of WTP 9. Nevertheless, the treatability of all WTPs for the MDMA FP removals were not affected by seasonal/temporal weather changes. On the other hand, the average THM FP removal efficiencies were somewhat higher during high rainfall periods probably due to the removal of additional THM precursors (i.e., mostly NOM) carried into WTPs during heavy rain periods (**Figure C.6**).

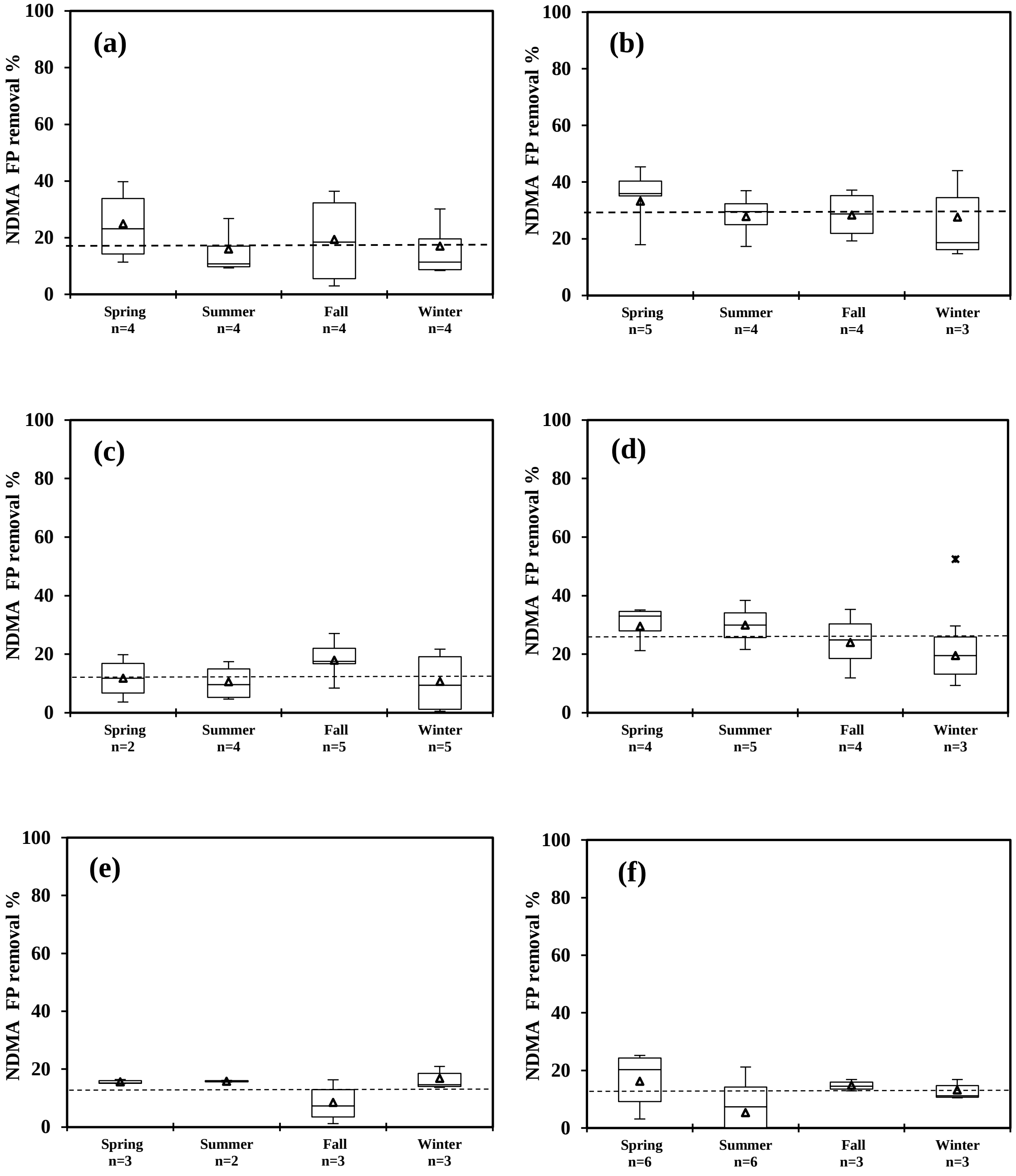


Figure 6.4. NDMA FP removals during different seasons at WTPs (a) 1, (b) 2, (c) 3, (d) 6, (e) 7 and (f) 9. Dotted lines denote the average NDMA removal of all measurements at each WTP. n denotes # of data.

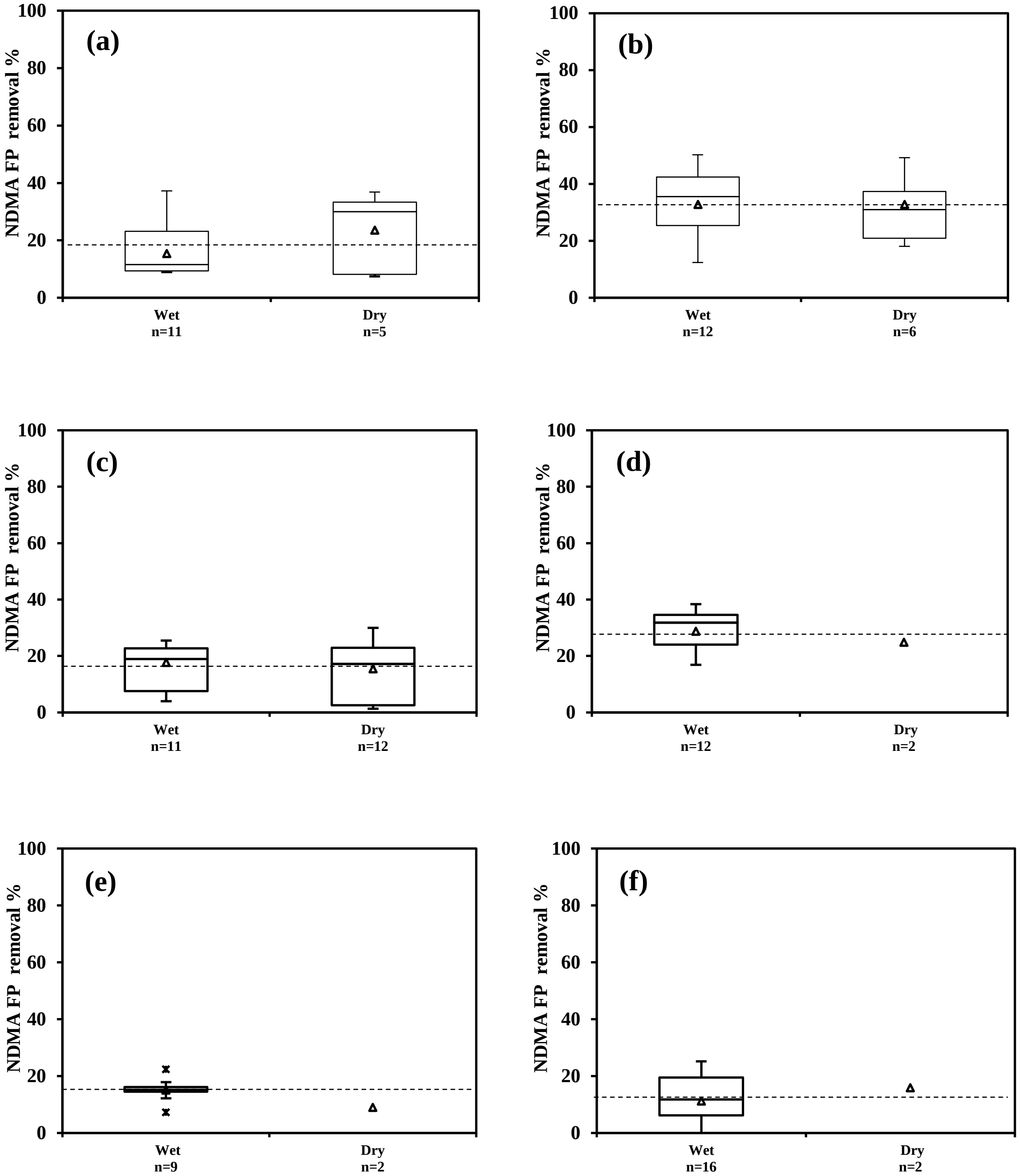


Figure 6.5. Comparison of NDMA FP removal efficiencies at WTPs (a) 1, (b) 2, (c) 3, (d) 6, (e) 7 and (f) 9 during wet (i.e., having rainfalls above the historical regional average 0.13 inch/day) versus dry (i.e., having rainfalls below 0.13 inch/day) rainfall periods. Dotted lines denote the average NDMA removal of all measurements at each WTP. n denotes # of data.

The Effects of PAC on NDMA FP Removals

PAC was used for taste and odor control at WTPs 2 and 3 during conventional clarification. Selected characteristics of PACs used at those WTPs are given in **Table C3**. During the entire sampling period, WTP 2 applied 4-8 mg/L of PAC for three times and WTP 3 applied 1-10 mg/L for six times. The removals of NDMA FP and THM FP with and without PAC addition were analyzed and plotted in **Figures 6.6** and **C.7**, respectively. At both WTPs, more NDMA FP removals were achieved when PAC was applied. In the absence of PAC, average NDMA FP removals were 30% and 13% which were attributed to alum clarification at WTPs 2 and 3, respectively (**Figure 6.6**). Addition of PAC apparently increased NDMA FP removals (from 30% to 46% at WTP 2 and from 13% to 28% at WTP 3) (Beita-sandi et al., 2016). A correlation (R^2=0.71) was observed between NDMA FP removal and PAC dose (**Figure 6.7**). However, for the range of 1-4 mg/L PAC applied, NDMA FP removals were not significantly higher than those achieved by alum alone. Therefore, it is suggested to dose PAC at more than 4 mg/L during conventional clarification in order to gain additional NDMA FP removals. In contrast, the impact of PAC on the THM FP removal was not significant indicating that alum clarification removes most NOM which is the main precursor of THMs, and addition of PAC does not cause further removal of THM FPs (**Figure C.7**). The impacts of PAC on NDMA FP removals were site-specific and thus further investigation on the benefit of PAC application under various operational conditions of treatment plants is warranted.

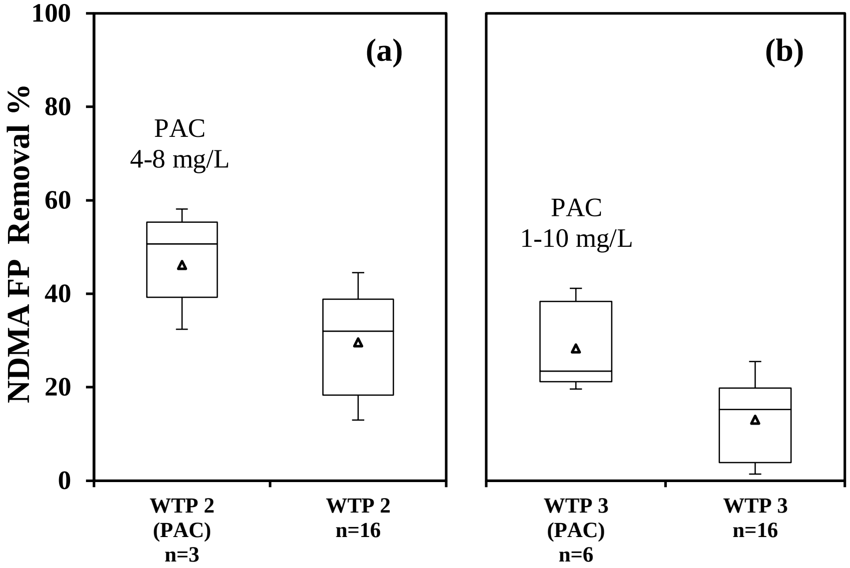


Figure 6.6. NDMA FP removals with and without PAC application at (a) WTP 2 and (b) WTP 3. n denotes # of data.

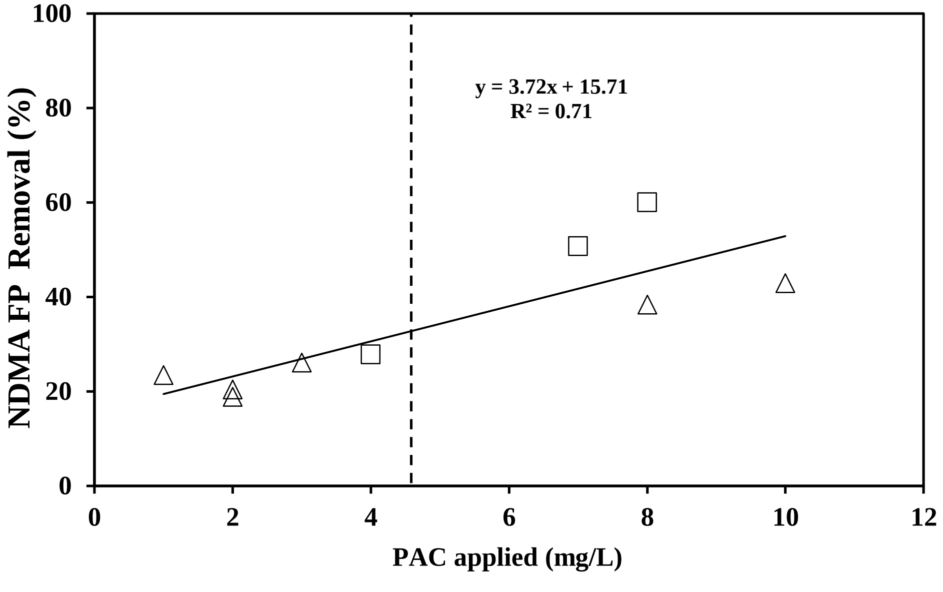


Figure 6.7. NDMA FP removals by PAC at WTPs 2 and 3. NDMA FP removals with PAC doses at WTP 2 and WTP 3 were shown with square (PAC applied 7, 4 and 8 mg/L at June 12, Aug 13, and Feb 14, respectively) and triangle (PAC applied 8, 2, 2, 10, 1, and 3 mg/L at Apr 12, May 12, Jul 12, Apr 13, Aug 13 and Feb 2014, respectively), respectively.

The Effects of Pre-oxidation on NDMA FP Removals

WTPs 1, 4, 5 and 8 employed pre-oxidation processes with Cl_2 (with/without ClO_2) and NH_2Cl. WTP 1 occasionally used Cl_2 at 0.4-0.9 mg/L as “a maintenance dose” to minimize microbial growth in treatment tanks and conduits. The impact of pre-chlorination on the removal of NDMA FP was negligible; average NDMA FP removal efficiencies were about 17% whether Cl_2 was added (n=10 months) or not (n=7 months) (**Figure 6.8a**). Although chlorination has been known to be an effective way for the control of NDMA precursors (Chen and Valentine, 2008; Krasner et al., 2008; Sacher et al., 2008; Shah et al., 2012), such low concentrations of Cl_2 did not lead to measurable NDMA FP removals probably due to less available chlorine as a result of the reaction between relatively high background DOC in raw water and chlorine (**Table 6.2**).

At WTPs 4 and 5, not only pre-oxidants (both Cl_2 and ClO_2) but also polymer (Sedifloc 400C) and PAC were always added at the beginning of treatment. Therefore, the impact of pre-oxidation at those WTPs on the NDMA FP removal was not clearly separated from the combination of all components. At WTP 4, 1.1 mg/L of ClO_2 and 0.4-1.1 mg/L of Cl_2 were typically used, while 0.4-1.9 mg/L of ClO_2 and 0.4-1.4 mg/L of Cl_2 were used at WTP 5. According to the jar test polymer experiment results, polymer Sedifloc 400C has the potential to contribute about 20 ng/L (at polymer dose 0.2 mg/L) to NDMA FP in natural waters (**Figure 6.2b**). Therefore, for the removal calculations, 20 ng/L (for polymer dose of 0.2 mg/L) was added to the NDMA FP levels in the influents of these two WTPs to reflect the polymer contributions. Typically, 2-3 mg/L PAC was applied at both plants, which is not a significant contributor to the NDMA FP removal. However, the combination of pre-oxidants (i.e., Cl_2 and/or ClO_2) and PAC reduced a substantial amount of NDMA FP with an average of 51% and 61% at WTPs 4 and 5, respectively (**Figure 6.8b**). At WTP 8 where NH_2Cl (2.5 mg/L) was added as a pre-oxidant, the average NDMA FP removal was only ~10% which might be attributed to the effect of alum clarification alone indicating that the contact of Cl_2 and/or ClO_2 prior to NH_3 addition is critical for deactivation of NDMA precursors (**Figure 6.8b**). The relatively high NDMA FP removals observed at WTPs 4 and 5 can be mainly attributed to the simultaneous application of ClO_2 and Cl_2 as pre-oxidants because alum clarification processes or PAC application at low concentrations (≤4 mg/L) would not lead to such high levels of NDMA FP removals.

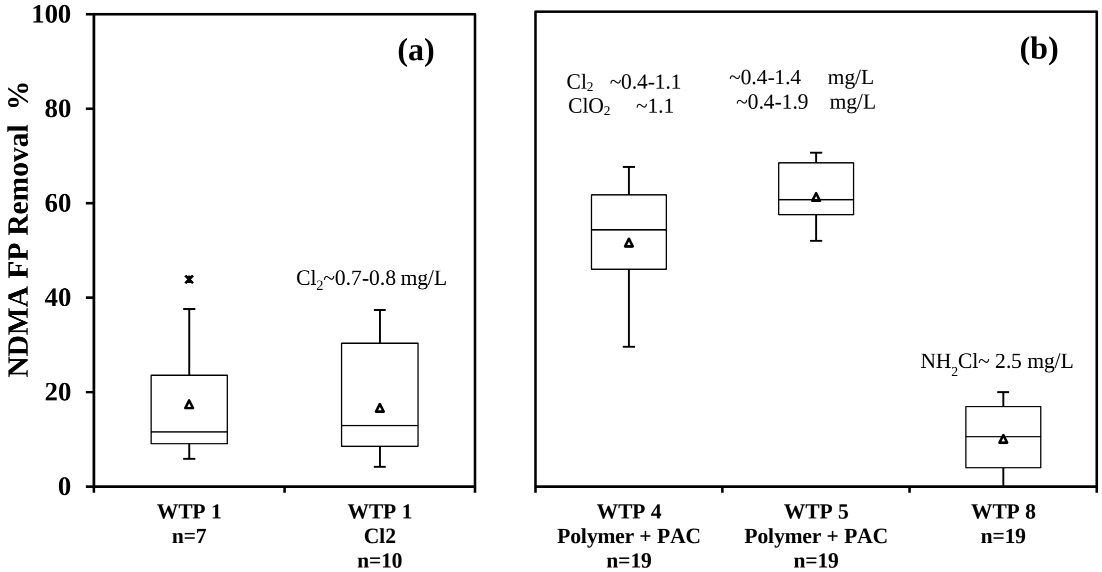


Figure 6.8. Comparison of NDMA FP removal with and without pre-oxidation at (a) WTP 1 and (b) the impact of pre-oxidation on NDMA FP removal at WTPs 4, 5, and 8. n denotes # of data.

The Effects of Post-oxidation with Cl_2 and/or ClO_2 on NDMA FP Removals

WTPs 2, 6, 7, and 9 treated raw waters without addition of any pre-oxidants, and WTP 1 did not apply pre-oxidation (n=7 months). Thus the effect of post-oxidation with Cl_2 alone prior to NH_3 addition was examined at those WTPs without interference of pre-oxidation effect on the NDMA FP removal. Ct values were determined by multiplying Cl_2 residuals in clearwell effluent by contact time. Most utilities maintained certain levels of target residual in the clearwell effluents to comply with the Ct requirement while not exceeding the maximum permissible level for the regulated DBPs (**Table C.4**). Average chlorination Ct values for WTPs 1, 2, 6, 7, and 9 were 355, 373, 332, 245, and 160 mg*min/L, respectively (**Figure C.8**). Average NDMA FP removals achieved by post-oxidation with Cl_2 ranged from 26 to 45% (**Figure 6.9a**). The NDMA FP removal as a function of Ct values was plotted for each plant (**Figure C.9**). The results showed no apparent correlation between Ct and NDMA FP removals at any WTPs, indicating that NDMA FP removal efficiencies already reached the maximum levels at relatively low Ct values and further removals may not occur with increasing Ct. It is also noteworthy that increased chlorination did not provide consistently high degrees of NDMA FP removals.

Further study on the effect of post-oxidation was conducted at WTP 3, because unlike the other WTPs, WTP 3 used ClO_2 with/without Cl_2 for post-oxidation prior to NH_3 addition without pre-oxidation processes. At this plant, the filtered main flow was split into two clearwells having different capacities. Approximately 80% of the flow entered clearwell #1, and 20% entered clearwell #2 (**Figure C.10**). To obtain Ct credit, ClO_2 (0.4-0.8 mg/L) was applied after the filters in two parallel clearwells for the first six month of the study. Then, the plant started to use supplemental Cl_2 (0.4-0.9 mg/L) in addition to ClO_2 in both trains. After the required Ct credit was achieved, Cl_2 and NH_3 were added simultaneously to form chloramines in the effluents of two clearwells. During months with ClO_2 application without Cl_2 addition, average removals of NDMA FP in the effluents of the two clearwells were ~27 % (**Figure 6.9b**), while their average Ct values were 15 mg*min/L at clearwell #1 and 45 mg*min/L at clearwell #2.

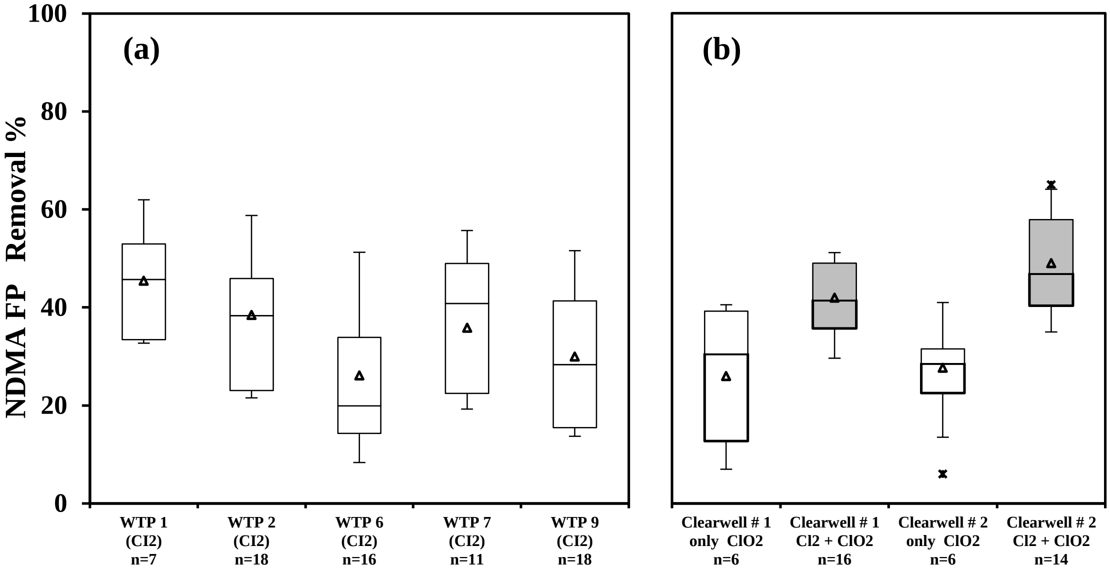


Figure 6.9. The effect of post-oxidation with (a) Cl_2 only at WTPs without pre-oxidation processes and (b) ClO_2 only vs. Cl_2+ClO_2 on NDMA FP removals at WTP 3. Clear boxes indicate only single oxidant (Cl_2 or ClO_2) applied as post-oxidant. Grey boxes indicate Cl_2 and ClO_2 applied simultaneously at WTP 3. n denotes # of data.

This result indicates that deactivation of NDMA precursors with ClO_2 may occur within a short time period, which is in good agreement with the results from previous studies (Lee et al, 2007; Shah et al, 2012; Selbes et al., 2014), and consequently high Ct conditions would not achieve any further deactivation of NDMA precursors. Furthermore, the simultaneous application of ClO_2 and Cl_2 increased NDMA FP removals in both clearwell effluents (i.e., from 27% to 42% in clearwell #1 and to 49% in clearwell #2).

NDMA Occurrences in Distribution Systems

According to the Stage 2 D/DBP Rule developed by USEPA, compliance with the maximum contaminant levels for THM and HAA_5 is calculated using the LRAA for each monitoring location in the distribution system. The same approach was adopted for NDMA occurrences, and LRAAs of NDMA in the distributions systems of nine WTPs are presented in **Figure 6.10.**

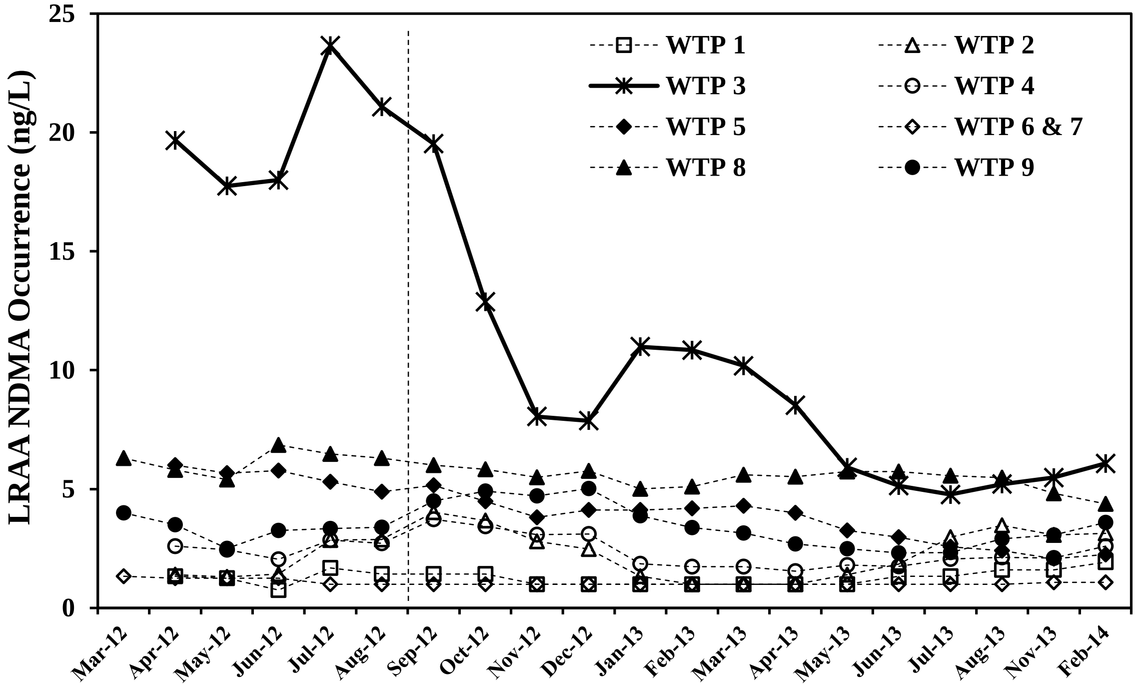
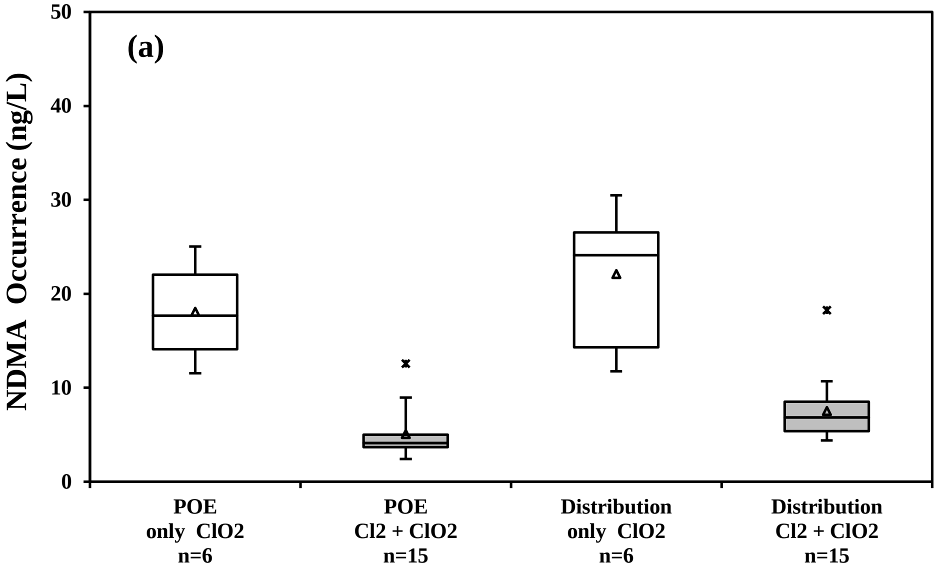


Figure 6.10. LRAA of NDMA occurrences in distribution systems. Dashed line indicates the dates when supplemental Cl_2 addition to ClO_2 for post-oxidation began at WTP 3.

LRAAs values were determined by taking averages of four consecutive data points (**Appendix C**). Except for WTP 3, NDMA occurrence levels were always below 10 ng/L of the California's notification level (CAEPA, 2013) in all WTPs consistently under their normal operation conditions. Interestingly, LRAAs in the distribution system of WTP 3 were significantly higher than those in other WTPs for the first six months of the study, and then dramatically decreased near or below 10 ng/L for the rest of the study period. WTP 3 applied ClO_2 as the post-oxidant before chloramination for the first six months, while supplemental Cl_2 was used with ClO_2 afterward and nothing else regarding the plant operations was not changed indicating that the simultaneous application of Cl_2+ClO_2 had a positive impact on reducing NDMA formation. Measured NDMA occurrences in the POE (from 18 ng/L to 5 ng/L) and the distribution systems (from 22 ng/L to 8 ng/L) of WTP 3 also showed dramatic changes caused by switching post-oxidation strategy (**Figure 6.11a**). However, THM formation in the POE and distribution system increased by about 70% (**Figure 6.11b**).

In addition to NDMA occurrences, FP tests were performed with samples collected at the POE and distribution system of WTP 3. NDMA occurrences were divided by NDMA FPs to obtain NDMA precursors' conversion rates for two different post-oxidation strategies (i.e., ClO_2 alone versus Cl_2+ClO_2) (**Figure 6.12a**). Approximately 55% of NDMA precursors converted to NDMA at the POE when ClO_2 was applied for post-oxidation before chloramination and no further formation was observed at the longest distribution point, indicating that the NDMA formation rates were very fast at WTP3.



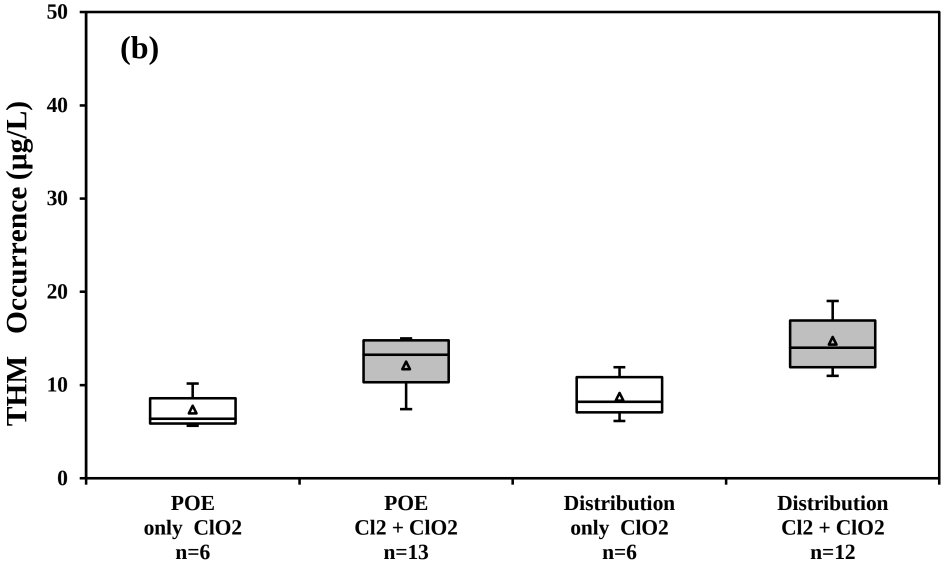


Figure 6.11. The effect of supplemental Cl_2 application to ClO_2 on (a) NDMA and (b) THM occurrences in the POE and distribution system of WTP 3. Clear boxes indicate only ClO_2 applied as post-oxidant. Grey boxes indicate Cl_2 and ClO_2 applied simultaneously at WTP 3. n denotes # of data.

When supplemental Cl_2 was added in addition to ClO_2 during water treatment, the NDMA conversion rates were significantly reduced at the POE (59%) and in the distribution system (42%) of WTP 3. The NDMA precursors' conversion rates in the distribution systems of the other WTPs varied from 8% to 35% depending on the characteristics of the source waters, detention time in the distribution systems and operational conditions (i.e., pre-/post-oxidation) (**Figure 12b**).

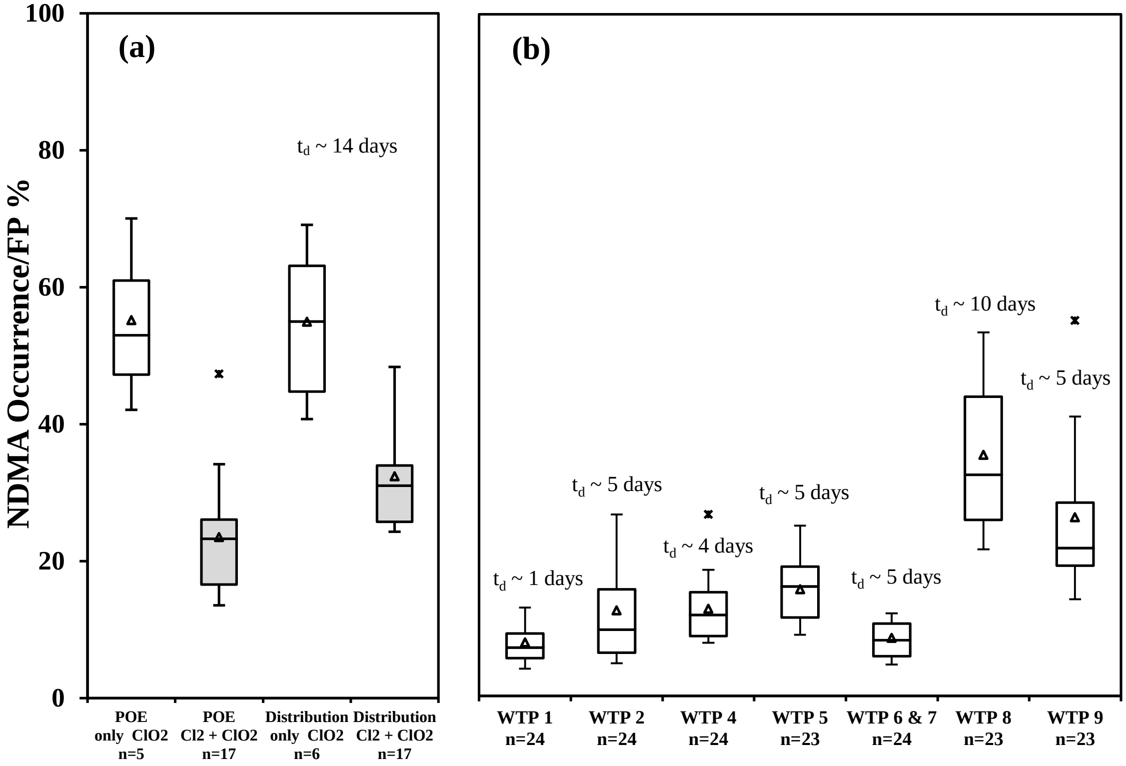


Figure 6.12. NDMA precursor conversion ratios (i.e., NDMA occurrence/NDMA FP) in (a) POE and distribution system of WTP 3 for two different post-oxidation strategies and (b) WTPs 1, 2, 4, 5, 6 &7, 8, and 9. Clear boxes indicate only single oxidant (Cl_2 or ClO_2) applied as post-oxidant. Grey boxes indicate Cl_2 and ClO_2 applied simultaneously at WTP 3. n denotes # of data.

NDMA FP Removals by Membranes

WTP 1 operated a RO unit occasionally and WTP 7 used a MF membrane (Pall) unit before clearwells. NDMA FP removals by RO and MF filtration ranged from 70 to 88% (average 81%) and from -4 to 20% (average 7%), respectively (**Figure 6.13a**). THM FP removals by RO ranged from 76 to 95% (average 88%), while they were between -2 and 21% (average 11%) by MF (**Figure 6.13b**).

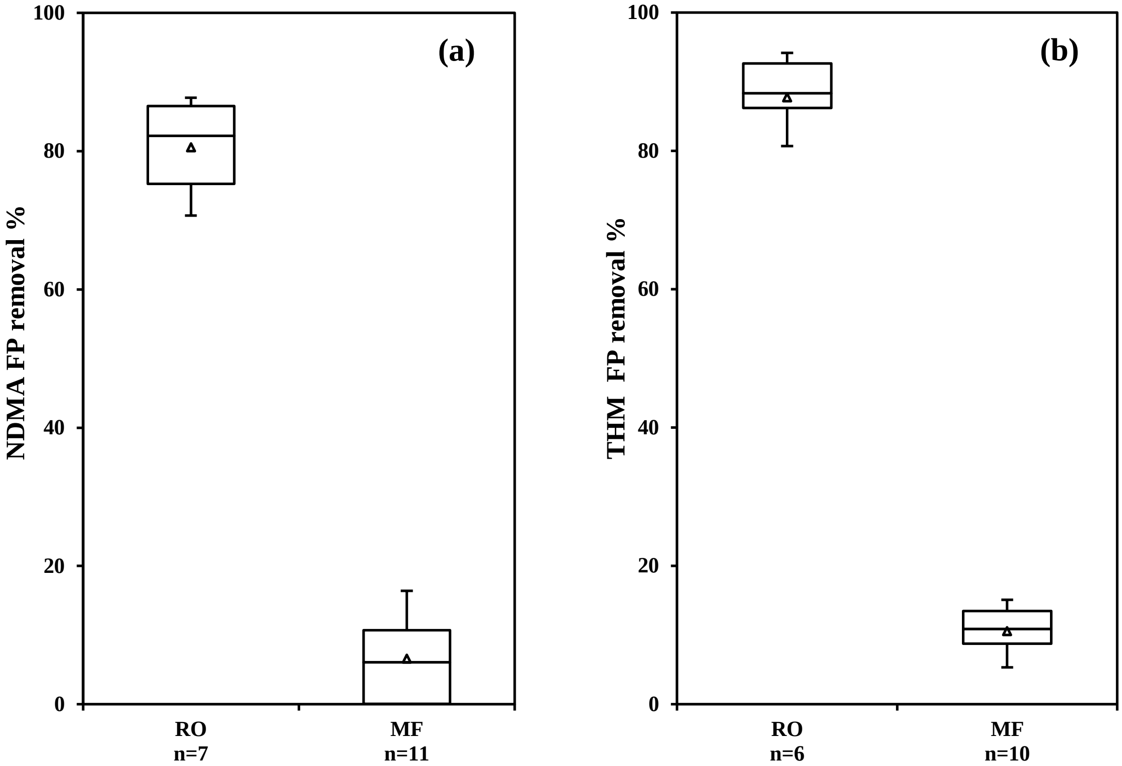


Figure 6.13. Removals of (a) NDMA FP and (b) THM FP by RO and MF**.** n denotes # of data.

MF is a separation process typically using membranes with molecular weight cut off (MWCO) mostly greater than 100,000 Da, while the typical range of MWCO is less than 100 Da for RO membranes. Therefore, the bulk portion of NDMA precursors might be removed more effectively by the RO filtration than MF. The NDMA FP removal was not efficient by MF at a full-scale WTP, which is consistent with the previous findings that NDMA precursors consist of mostly small molecular weight compounds (<3000 Da) (Mitch and Sedlak, 2004; Pehlivanoglu-Mantas and Sedlak, 2008; Krauss et al., 2010).

Conclusions

This long term monitoring study has shown that polymer type and/or dose, PAC application, and oxidation practices affected the NDMA FP removals at full-scale WTPs. An average NDMA FP removal efficiency of alum clarification alone was 12-30% and different seasons and various weather conditions did not affect significantly the removal efficiencies of NDMA FP. When PAC was applied at more than 4 mg/L and the simultaneous application of Cl_2 + ClO_2 was used for pre-/post-oxidation, additional removals of NDMA FP were achieved. Although the overall removal efficiencies of NDMA FP between raw water and POE in most WTPs were 40-59%, NDMA occurrences were below 10 ng/L which is California's notification level while complying with the Stage 2 D/DBP Rule. Therefore, extra treatment processes are required especially for WTPs that have relatively high influent NDMA FP levels and/or use polymers yielding high NDMA FP to control more effectively NDMA formation at chloraminated distribution systems.

CHAPTER SEVEN

REMOVAL OF NDMA FP IN WASTEWATER-IMPACTED WATERS BY ClO_2 OXIDATION AND THE EFFECT OF OXIDATION pH

Introduction and Objectives

Over 600 DBPs have been reported in simulated laboratory disinfections or disinfected drinking waters, resulting from the use of oxidants, notably chlorine, chloramines, ozone and chlorine dioxide (Bond et al., 2011). Due to the health concerns and noticeable occurrences, there has been an increasing regulatory attention on nitrosamines by the USEPA. Since NDMA is the most commonly detected nitrosamine species in US distribution systems (Russel et al., 2012; Woods et al., 2015), this chapter focused on the control of NDMA formation.

The primary source of amine precursors of NDMA is known to be anthropogenic (Sacher et al., 2008; Schreiber and Mitch 2006; Bond et al., 2011; Shen and Andrews 2011; Le Roux et al., 2011; Uzun et al., 2015), in contrast with the regulated THMs and HAAs, for which NOM constitutes the main precursor pool. Higher NDMA precursor concentration levels in WW-impacted water sources with higher pharmaceutical levels (e.g., primidone, carbamazepine) support this assessment (Schreiber and Mitch 2006). Moreover, treated municipal WW discharges increased from 1980 to 2008 in some of the US surface waters (Rice et al., 2013), and NDMA FPs at the intake locations might be influenced by an upstream WWTP effluent discharge in river systems (Uzun et al., 2015). However, depending on the degree of applied WW treatment, the amount of dilution and the effect of natural attenuation on NDMA precursors during transportation, precursor loadings may vary at intakes of drinking water treatment facilities.

Considering the effectiveness of conventional oxidants (i.e., ClO_2 and Cl_2,) (Lee et al., 2007; Sacher et al., 2008; Shah et al., 2012; Krasner et al., 2015), pre-oxidation can be a plausible way to deactivate NDMA precursors before chloramine addition during water treatment. Recently, the effects of ClO_2 oxidation on the removal of NDMA FP or NDMA formation have been widely investigated, but the results have not been consistent with each other. Up to 94% NDMA FP removals were reported when ClO_2 was applied at ~2.7 mg/L for 5-10 min contact time to raw water samples (Lee et al., 2007; Sacher et al., 2008). However, when ClO_2 was applied to model compounds whose NDMA yields are less than 3%, DMA was released as a by-product and consequently increased NDMA formation (Lee et al., 2007; Selbes et al., 2014) compared to the parent compounds. In a study conducted by Shah et al. (2012), ClO_2 oxidation prior to chloramination showed a negligible effect on NDMA formation in treated water samples (i.e., collected samples after conventional treatment processes prior to any oxidant addition). Inconsistent findings in a number of studies on the effectiveness of ClO_2 oxidation on the deactivation of NDMA precursors may be related to the differences in the characteristics of tested waters (e.g., WW-impacted or non/low impacted surface waters, polymer and anion exchange impacted treated waters, etc.), and different oxidation conditions (e.g., oxidant dose, pH, Ct, etc.).

The literature summary presented in **Table 7.1** shows that ClO_2 oxidation before chloramination reduced NDMA formation in most WW impacted waters. Since oxidation conditions such as oxidation pH, ClO_2 dose, and used water types were not carefully investigated in terms of NDMA FP removals, it is not easy to draw general conclusions with known results.

During drinking water treatment, ClO_2 can be used at different locations for the disinfection. The main mechanism of the reaction of ClO_2 with organic compounds has been known as free radical abstraction and electron transfer without the cleavage of carbon-carbon bonds and addition of chlorine to organic molecules (Körtvélyesi, 2004). An early study conducted by the American Water Works Service Company showed a reduction of THMs (59-90%) using ClO_2 instead of chlorine (Blanck, 1979). Following studies have shown that ClO_2 can form considerable amounts of HAA species (up to 19.3 µg/L) (Zhang et al., 2000), however, none or trace amount (up to 5 µg/L) of THM formation has been reported (e.g., Richardson et al., 1994; Zhang et al., 2000; Gates et al., 2009).

ClO_2 as an electron acceptor, can react with both inorganic and organic compounds containing lone pair electrons or p electrons and attacks the electron-rich centers of organic molecules (Gates et al., 2009) such as amines which may serve as NDMA precursors. ClO_2 reaction rates with amines increased with increasing pH, and the reaction rates were accelerated with neutral tertiary amines (Lee et al., 2007; von Gunten et al., 2010). Moreover, the reactivity of amines with ClO_2 follows the order of tertiary > secondary > primary amines (Rosenblatt et al., 1967). The reaction of amines with ClO_2 occurs in two steps. Intermediates resulted from either a hydrogen abstraction mechanism or an electron transfer from the nitrogen atom of the amine to ClO_2 (Rosenblatt et al., 1967). Principal rate-controlling step in the reaction of tertiary amines is known to be the electron-transfer process rather than the hydrogen abstraction process (Hull et al., 1967).

Table 7.1. Effects of ClO_2 oxidation on NDMA FP and NDMA formation – Literature summary.

	Waters	ClO_2 (dose)	Ct or T_d	Oxidation pH	Removal (%)	Key Findings	Reference
Wastewater impacted waters	Surface Water	2.7 mg/L	5 min	7.0	Up to ~90 %	○ ClO_2 pre-oxidation was effective on removal of NDMA FP. ○ ClO_2 were very effective on removal of nitrosamines precursors at river and lake waters.	Lee et al., 2007; Sacher et al., 2008
	Surface Water	2 mg/L	0-25 mg*min/L	7.1	50%	○ NDMA formation decreased about 50% at the 5 mg*min/L, then there is no significant difference with the increasing Ct.	Shah et al., 2012
	Surface Water		0-22 mg*min/L	8.3	40%	○ NDMA formation decreased about 40% at the 5 mg*min/L, then there is no difference with the increasing Ct.	
	Softened Water		0-20 mg*min/L	8.0-8.5	Negative removal	○ NDMA formation continuously increased with increasing Cts.	
	2 Secondary Effluent	1 mg/L	N/A	7.0	58%	○ Pretty good amount of NDMA FP removal observed in both of wastewater impacted waters (50-70%).	Yang et al., 2013
Other waters	Poly DADMAC impacted	2 mg/L	0-32 mg*min/L	7.2	Negative removal	○ NDMA formation continuously increased with increasing Cts.	Shah et al., 2012
	Anion exchange resin impacted		0-10 mg*min/L	7.0	Negative removal	○ NDMA formation decreased about 40% at the 5 mg*min/L, then there is no significant difference with the increasing Ct.	
	Poly DADMAC impacted		0-20 mg*min/L	8.0	~40%	○ NDMA formation decreased about 40% at the 5 mg*min/L, then there is no significant difference with the increasing Ct.	
	12 Surface 1 Ground water	1 mg/L	N/A	7.0	Negative removal 50%	○ ClO_2 pre-oxidation decreased NDMA FP for most of the waters except two of them. ○ One of the surface water and ground water has shown increasing trend after ClO_2 oxidation.	Yang et al., 2013

N/A: Not available

Based on the literature summary, it was hypothesized that ClO_2 oxidation before chloramination may reduce NDMA formation in WW-impacted waters, and amine precursors can be deactivated better by ClO_2 oxidation at relatively higher pH compared to lower pH conditions. Furthermore, it is well known that natural attenuation processes can effect NDMA precursors (Beita-sandi et al., 2016). Therefore, the following factors were investigated in this chapter: (i) the effect of different SWs (e.g., WW impacted vs. low/non impacted waters), (ii) the effects of oxidation pH, oxidant dose, and Ct (mg-m/L) during oxidation with ClO_2 on NDMA FP and formation, and iii) the effect of natural attenuation on NDMA precursors that are reactive towards ClO_2. Such systematic investigation of ClO_2 & chloramines application conditions (i.e., applied water type, oxidation pH & dose & contact time, effect of natural attenuation) can guide researchers and practitioners to develop better strategies to minimize NDMA formation while complying USEPA D/DBPR, especially when WW-impacted source waters are in use.

Water Samples

Treated water samples were collected three times from WTP 3 when the utility was treating (a) 100% of SW E (~1-2 % upstream treated WW-impacted) which is labeled as treated water (TW) E, (b) 100% of SW D which is labeled as TW D, and c) a treated mixture (40:60) of SW E and SW D. During the collection of each sample, there was no use of pre-oxidant or PAC at the treatment plant. Another set of tested waters was prepared by mixing SW I (non-impacted lake water) with effluent water (EW) 1 of WWTP 1 to create 10-50% impacted lake water samples (**Figure 7.1a**).

SW O (upstream of WWTP 2 discharge point) was mixed with EW 2 of WWTP 2 to create 10-50% impacted waters (**Figure 7.1b**). Measured NDMA FP, THM FP, and selected water quality parameters of the tested waters showed a wide range of characteristics (**Table 7.2**). DOC, specific ultraviolet absorbance at 254 nm ($SUVA_{254}$), DON and bromide values were 1.7-7.6 mg/L, 1.9-5.2 L/mg-m, 14-95 µg/L, and 0.12-2.4 mg/L, respectively. NDMA FPs ranged from 36 to 1602 ng/L, while THM FPs were between 249 and 399 µg/L.

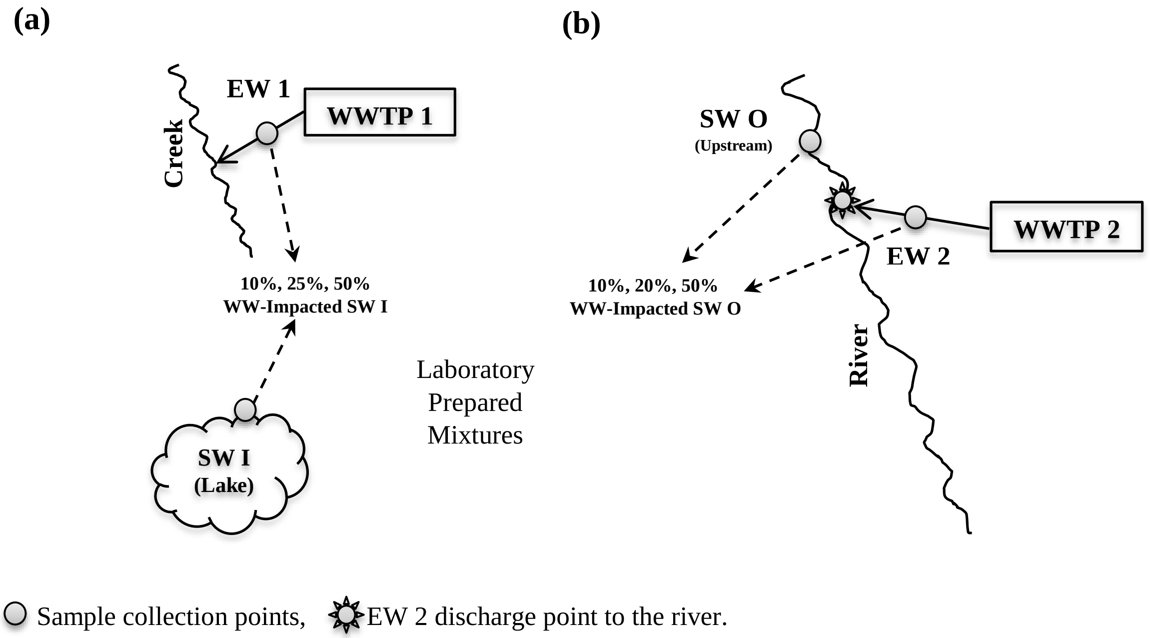


Figure 7.1. Preparation of WW-impacted (a) SW I and (b) SW O samples. EW 2 impact on the river was 18% (calculated by the ratio of EW 2 discharge flow to the total river flow [SW O]) during the day of sample collection.

Table 7.2. Water quality parameters of waters used during ClO_2 experiments.

Code	Water type	DOC (mg/L)	$SUVA_{254}$ (L/mg-min)	Bromide (µg/L)	DON (mg/L)	THM FP (µg/L)	NDMA FP (ng/L)
TW E	WTP 3 100% SW E (treated water)	4.8	1.9	15	0.20	399	42
TW D	WTP 3 100% SW D (treated water)	4.4	1.3	60	0.25	385	35
SW I	Non/low impacted (lake water)	2.1	4.9	14	0.26	249	36
SW O	Upstream of WWTP2 (creek water)	1.7	5.2	24	0.12	N/M	64
EW 1	WWTP 1 effluent water	3.1	2.1	65	2.1	290	605
EW 2	WWTP 2 effluent water	7.6	2.1	95	2.4	N/M	1602

N/M= not measured.

ClO_2 Application

In natural waters, 50-70% of ClO_2 is typically converted to chlorite (ClO_2^-) and the remainder is converted to chlorate (ClO_3^-) and Cl^- (USEPA, 1999). The D/DBPR set the maximum residual disinfectant concentration (MRDL) of ClO_2 at 0.8 mg/L, and the MCL of ClO_2^- at 1.0 mg/L. Therefore, the upper limit of ClO_2 dose was set at 1.4 mg/L in this study. The details of ClO_2 production is described in Chapter Four.

Pre-oxidation Experiments

Pre-oxidation experiments were conducted in 1 L amber glass bottles at room temperature (~21 ^oC) with ClO_2 (i.e., 0.7 or 1.4 mg/L of initial doses) for up to 90 min of contact time. The schematic diagram of the experimental matrix is shown in **Figure 7.2**. Experiments were conducted in duplicate at pH 6.0, 7.8, and 9.0 (only for selected samples) using 2 mM phosphate buffer and HCl or NaOH, as needed. Pre-determined ClO_2 was spiked into samples and residual ClO_2 was measured using HACH DR/820 colorimeter with DPD colorimetric test kits according to a HACH Method 10126. The residual ClO_2 was quenched with a stoichiometric amount of sodium thiosulfate at the end of the contact times. Prior to FP test, pH was adjusted to 7.8 by adding 20 mM phosphate buffer and NaOH (if needed). A pre-determined volume of NH_2Cl stock solution and Cl_2 stock solution (5-6% available free Cl_2) were spiked to achieve initial doses of 100 mg/L of NH_2Cl and 50 mg/L initial Cl_2 for NDMA FP and THM FP tests, respectively. After 5 days contact time at room temperature, residual oxidants (i.e., NH_2Cl [>25 mg/L] for NDMA FP and Cl_2 [>20 mg/L] for THM FP tests) were measured and quenched with sodium thiosulfate and sodium sulfite, respectively, before extractions.

In addition to FP tests, UFC tests were also conducted with NH_2Cl at 3 mg/L for 3-day contact time at pH 7.8 for selected samples to assess NDMA formation in distribution systems. No quenching agent was added to the UFC samples after ClO_2 oxidation. NDMA FP, THM FP and NDMA UFC tests were also conducted without ClO_2 oxidation as a control and the removal efficiencies were calculated based on the difference of the raw water (non-oxidized) and oxidized water`s results. Chemical standards, Ct calculation (**Appendix D**), analytical methods used for NDMA, THMs and other water quality measurements and ClO_2 production are described in Chapter Four.

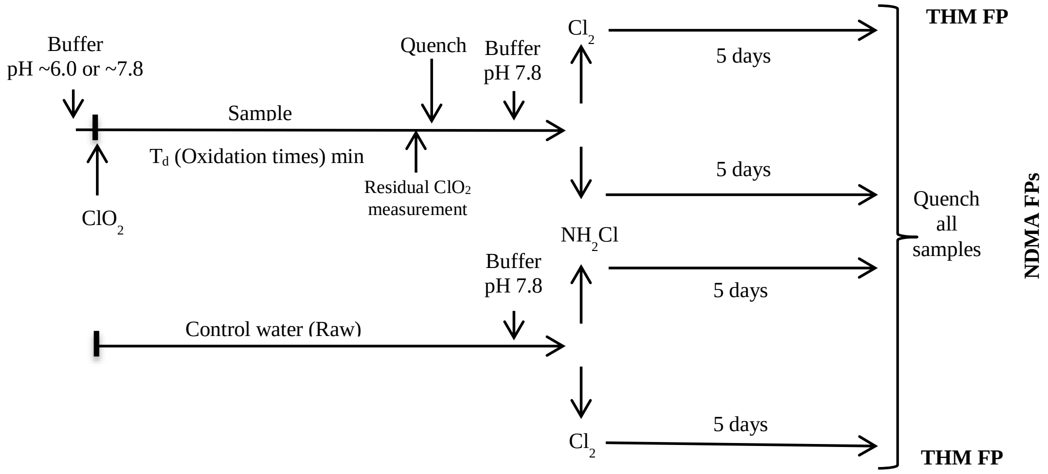


Figure 7.2. Experimental matrix of the ClO_2 experiments for FP tests.

Results and Discussions

Residual ClO_2 Concentrations after Oxidation

After pre-determined oxidation contact times, the residual ClO_2 concentrations were measured for selected waters. ClO_2 residuals (the initial dose of ClO_2=1.4 mg/L) as a function of time in TW E, TW D, SW I, and 25% WW-impacted SW I (i.e., 75% SW I + 25% EW 1) are shown in **Figure 7.3.** In TW E, observed ClO_2 residuals were 0.89 mg/L after 5 min and 0.32 mg/L after 90 min at pH 6.0, while the residuals decreased to 0.69 mg/L after 5 min and 0.15 mg/L after 90 min at pH 7.8 (**Figure 7.3a**). In TW D, ClO_2 consumption was faster and the residuals were 0.73 and 0.49 mg/L after 5 min, and 0.29 and 0.16 mg/L after 90 min at pH 6.0 and 7.8, respectively (**Figure 7.3b**). In both treated waters, ClO_2 consumptions increased as pH increased. In SW I, ClO_2 residuals were 1.3 and 0.93 mg/L after 10 min, and 0.84 and 0.60 mg/L after 90 min at pH 6.0 and 7.8, respectively (**Figure 7.3c**). Similar results were observed in 25% WW-impacted SW I where ClO_2 residuals were 1.23 and 0.91 mg/L after 10 min, and 0.90 and 0.61 mg/L after 90 min at pH 6.0 and 7.8, respectively (**Figure 7.3d**). Presented oxidant consumption trends indicated that the residual ClO2 decreased with extended oxidation time and increasing pH in natural waters. Relatively higher consumption rates at pH 7.8 can be attributed to enhanced ClO2 disproportionation and reactions with background organic compounds in natural waters under alkali conditions.

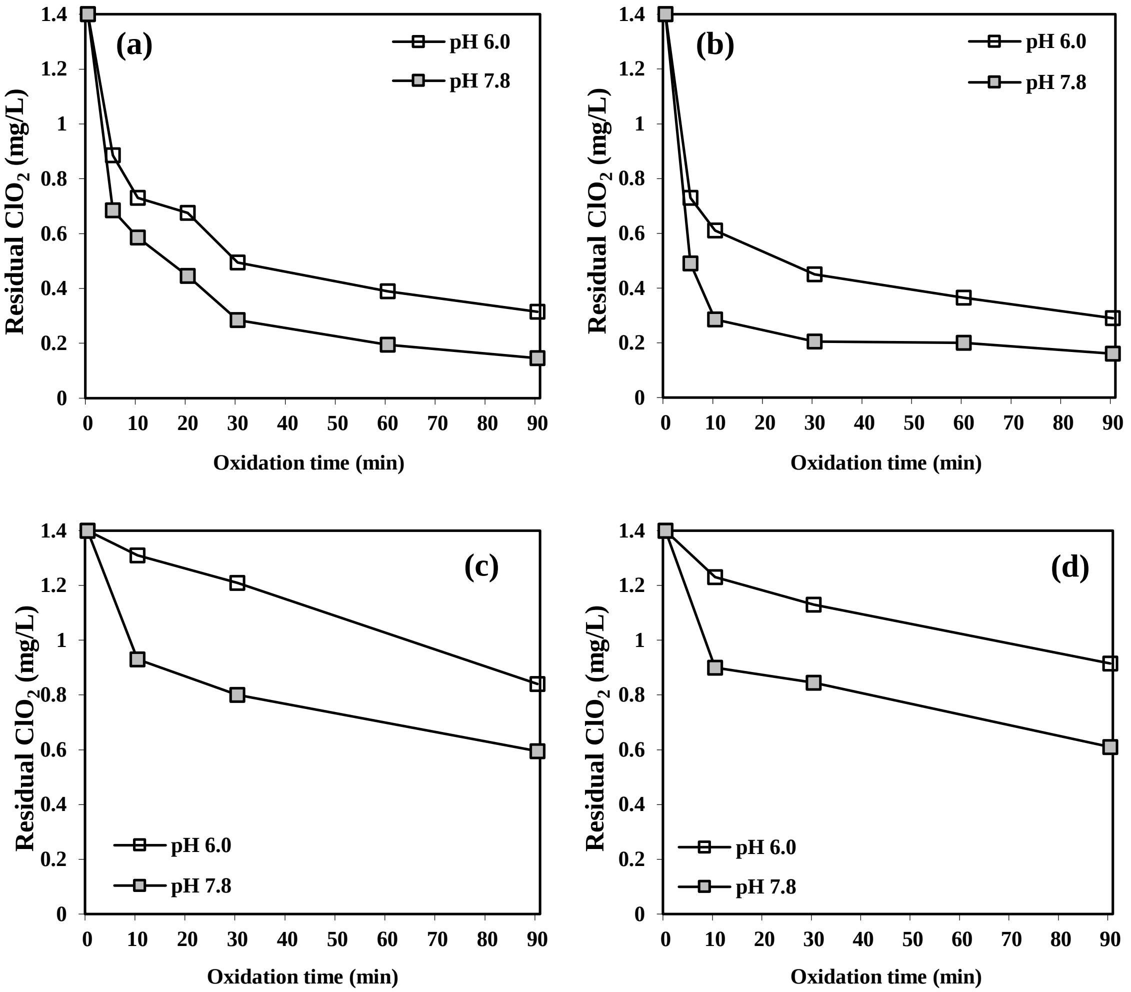


Figure 7.3. ClO_2 residuals of oxidation experiments for (a) TW E, (b) TW D, (c) SW I and (d) 25% EW 1 WW-impacted SW I. Initial ClO_2 dose=1.4 mg/L

These observations were in agreement with previously reported observations (Gates et al., 2009; von Gunten et al., 2010). Furthermore, increasing DOC concentration also increased the ClO_2 consumption for both pH oxidation conditions in TW E and TW D background waters compared to other waters tested (**Figure 7.3**). This was also in agreement with the study in which an empirical model for ClO_2 consumption based on bench-scale tests with six raw waters was conducted (Korn et al., 2002).

NDMA FP Removal by ClO_2 and the Effect of Oxidation pH

NDMA FP removals as a result of ClO_2 (1.4 mg/L) oxidation of TW E, TW D, mixture of 40% TW E + 60% TW D, and SW I are shown in **Figure 7.4.** The observed removals in TW E (WW-impacted) were 15% at pH 6.0 and 57% at pH 7.8 after 5 min, and then the removals remained similar by the end of the 90 min oxidation time (**Figure 7.4a**). The pre-oxidation pH played a key role in the removal of NDMA FP (i.e., significantly higher removals were observed at higher oxidation pH [i.e., 7.8]), while contact times longer than 5 min did not significantly impact removals. In TW D, NDMA FP removals for the initial 5 min were -13%, 7%, and 19% at pH 6.0, 7.8, and 9.0, and after 90 min of oxidation, the removals reached -4%, 25%, and 21%, respectively (**Figure 7.4b**). Negative removals indicate that NDMA FP increased after ClO_2 oxidation.

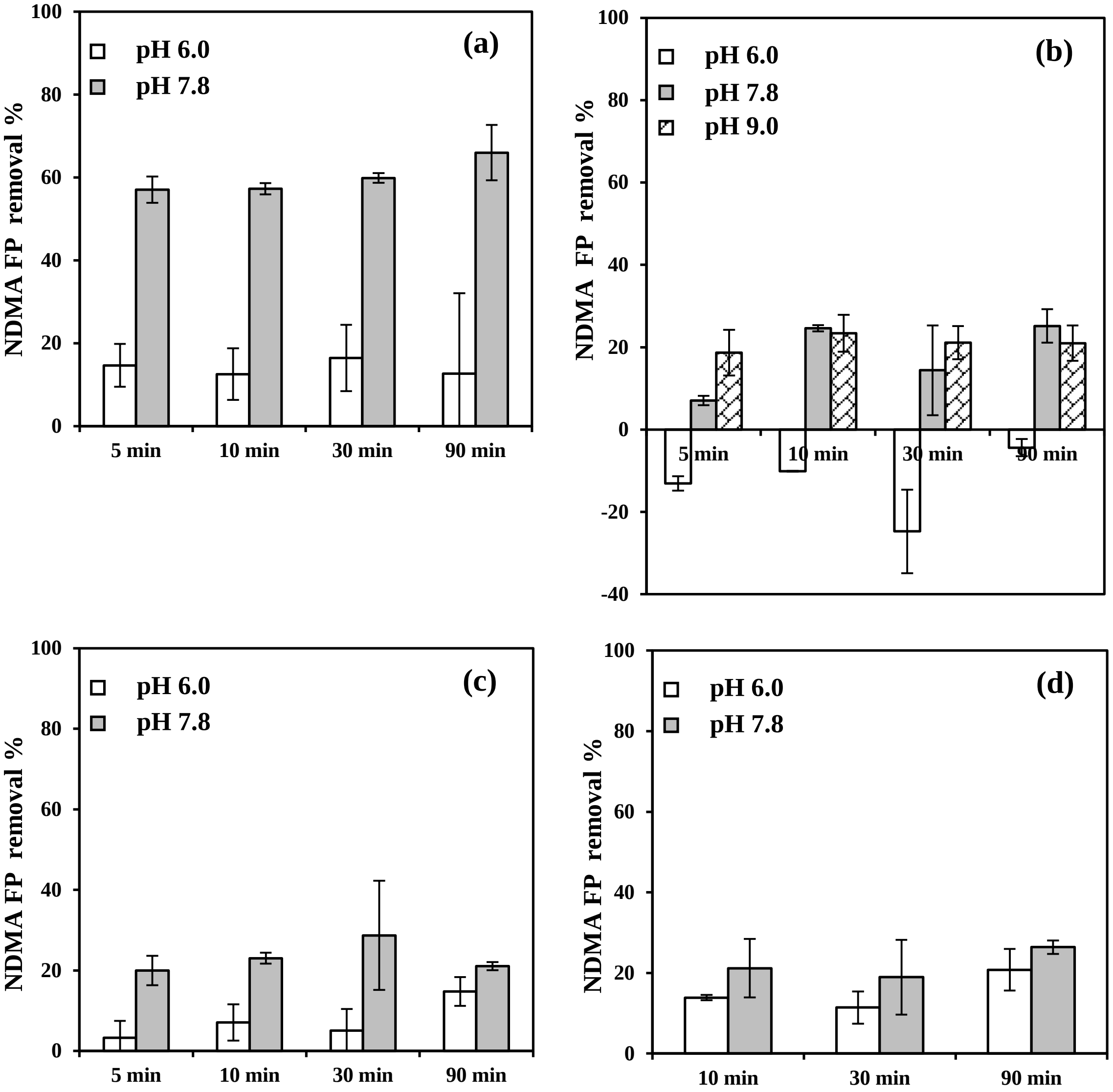


Figure 7.4. NDMA FP removals by ClO_2 oxidation from (a) TW E, (b) TW D, (c) mixture of 40% TW E + 60% TW D and (d) SW I. Initial ClO_2 dose=1.4 mg/L. Error bars represent data range for duplicate samples.

These results indicate that less reactive NDMA precursors are present in TW D since the effect of ClO_2 oxidation on the removal efficiencies was low (<25%). For the mixture of TW E & D, NDMA FP removals were between those from individual waters (i.e., TWs E and D) showing only 3% and 21% after 5 min, and 15% and 21% by the end of 90 min oxidation at pH 6.0 and 7.8 respectively (**Figure 7.4c**). In SW C, NDMA FP removals slightly improved at higher pH, however, the removals were <25% (**Figure 7.4d**). In laboratory mixed samples, NDMA FP removals were ≤25% in WW-impacted water at pH 6.0 (**Figure 7.5**). At pH 7.8, however, NDMA FP removals increased up to about 77% and 62% after 90 min contact times in WW-impacted SW I and SW O samples, respectively (**Figure 7.6**).

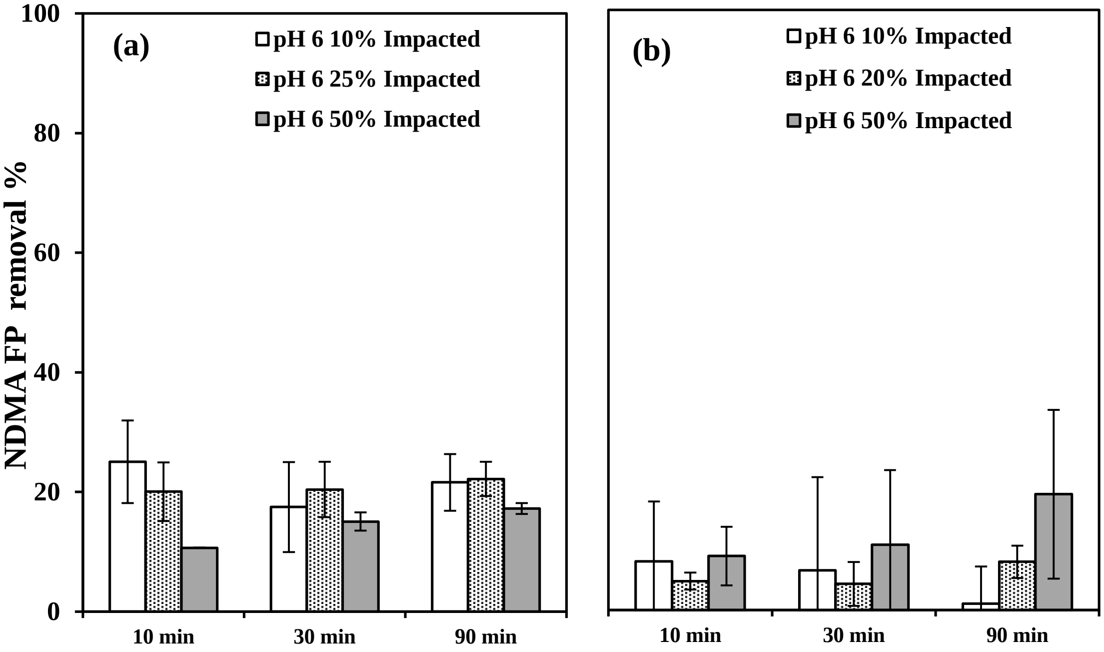


Figure 7.5. The effect of ClO_2 oxidation on NDMA FP at pH 6.0 in WW-impacted (a) SW I (b) WW-impacted SW O. Initial ClO_2 dose=1.4 mg/L. Error bars represent data range for duplicate samples.

Lower removal efficiencies observed in WW-impacted SW O than WW-impacted SW I water (pH 7.8) were attributed to higher background DOC levels of EW 2 used to prepare the WW-impacted samples (**Table 7.2**). These results further demonstrated that

ClO_2 oxidation is more effective at higher pH (i.e., 7.8) for removing NDMA FPs from WW-impacted waters. However, high background DOC levels may hinder the deactivation effect of ClO_2 due to either fast consumption or competition reactions.

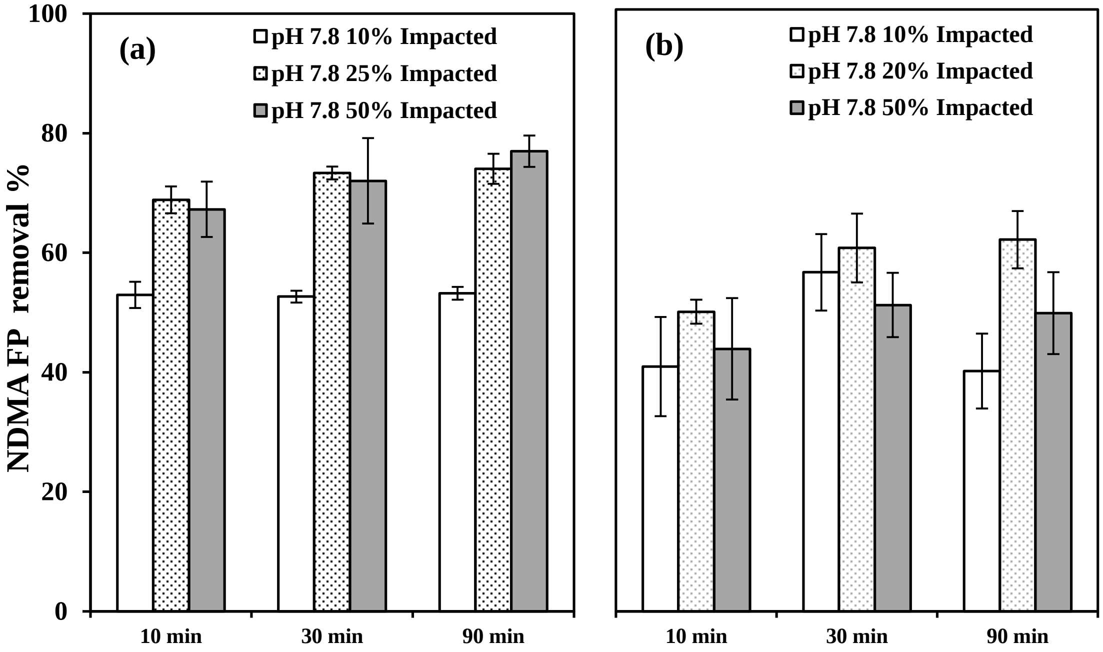


Figure 7.6. The effect of ClO_2 oxidation on NDMA FP at pH 7.8 in WW-impacted (a) SW I (b) WW-impacted SW O. Initial ClO_2 dose=1.4 mg/L. Error bars represent data range for duplicate samples.

To further investigate the pH effect, NDMA FP removals were examined with 20% WW-impacted SW O water prepared using EW 2 at four different oxidation pH values (i.e., 6.0, 7.0, 7.8, and 9.0). NDMA FP removals after 10 min of oxidation increased from 5% to 61% as pH increased from 6.0 to 9.0 (**Figure 7.7**). ClO_2 oxidation apparently increased NDMA FP removals with increasing pH from 6.0 to 7.8; however, further increase from 7.8 to 9.0 did not result in additional removals. These results indicate that an optimal ClO_2 oxidation pH is required to reduce NDMA FPs in WW-impacted surface waters. Ten minutes of oxidation was sufficient to obtain the maximum NDMA FP removals (>50%) in the WW-impacted waters tested at pH 7.8 and 9.0. However, only 30-60% of the maximum removals was obtained for the initial 10 minute of oxidation at pH 6.0 and 7.0.

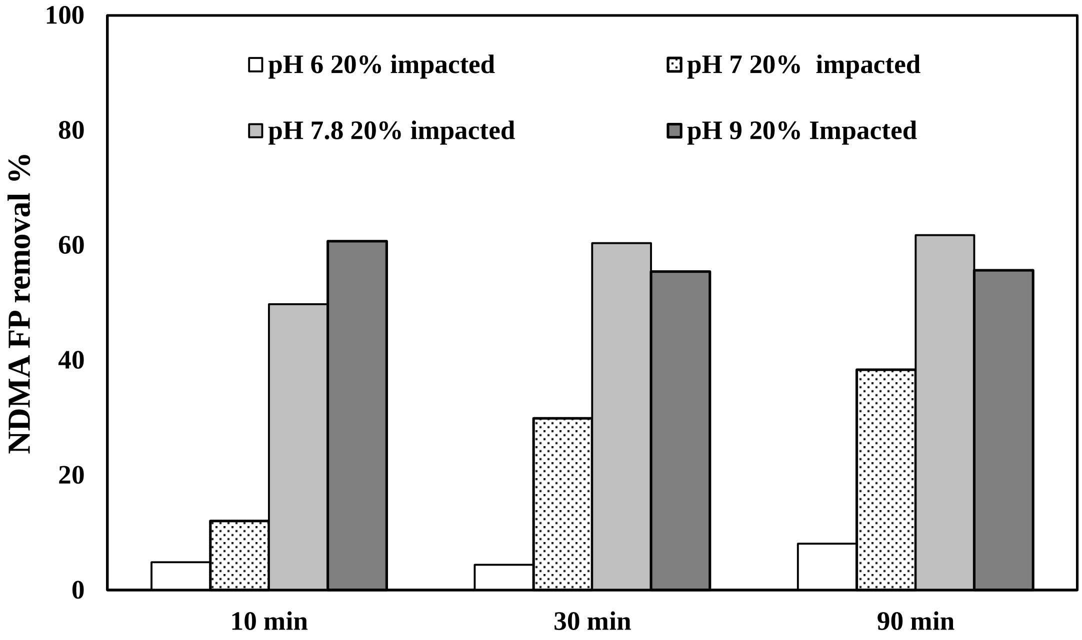


Figure 7.7. NDMA FP removal trends for low to high oxidation pH values (6.0-9.0) at 20% WW-impacted SW O. Initial ClO_2 dose=1.4 mg/L.

It has been shown that the tertiary amines react with ClO_2 to form organic and inorganic products and the reaction mechanism has been shown to be complicated and pH dependent (Rosenblatt et. al., 1967). Recently, it was reported that dimethylamine (DMA) is released from the reactions of model NDMA precursors (e.g., selected tertiary amines) with ClO_2. Therefore, for the tertiary amine precursors (e.g., ranitidine, N,N-dimethylisopropylamine, etc.) that yield more NDMA than DMA which typically yields is <3% during chloramination, pre-oxidation with ClO_2 can effectively reduce NDMA formation. (Lee et al., 2007; Selbes et al., 2014). However, if the NDMA yields of amine precursors (e.g., N,N-dimethylaniline, methylene blue, etc.) are relatively low (e.g., <2%), then NDMA molar conversions after ClO_2 oxidation will increase due to the formation of DMA (Selbes et al., 2014). NDMA FPs were reduced effectively at high pH ($\geq$ 7.8) in WW-impacted waters, indicating that treated WW effluent water examined for the study include relatively high yield (>3%) NDMA precursors whose molar yield is more than DMA released from the reactions between amine precursors and ClO_2.

Deactivation Mechanism of NDMA Precursors with ClO_2 Oxidation

ClO_2 reaction rates with amines increased with increasing pH (Lee et al., 2007, von Gunten et al., 2010). Selbes and colleagues (2014) interpreted this observation as an accelerated reaction of ClO_2 with deprotonated amines rather than protonated ones. Therefore, pKa values of amine precursors can be an important factor governing amine deactivation by pre-oxidation with ClO_2. According to the Henderson-Hasselbach equation, increasing pH increases the amount of deprotonated species. At a pH close to or higher than the amines' pKa values, ClO_2 could attack effectively deprotonated amines. It has been known that the reactions of ClO_2 with organic compounds occurred through electron transfer mechanism not substitution mechanism (Gates et al., 2009; Hull et al., 1967). Thus the presence of available electron pairs on the nitrogen atom of amine precursors can facilitate the reactions with ClO_2.

Figure 7.8 illustrates a possible reaction mechanism between ClO_2 and amine precursors. At relatively low pH (e.g., pH 6.0), ClO_2 cannot attack the lone pair electrons of the nitrogen atom of amine molecule since the reaction site is blocked by a hydrogen atom. As pH increases, however, deprotonation (step 1) occurs to produce amine species with lone pair electrons to be attacked by ClO_2 (step 2). As a result of the oxidation mechanism, ClO_2^- and an amine carbocation can be formed (step 3). Finally, carbocation intermediates can be further transformed to DMA and other products (step 4). Based on the proposed deactivation mechanism, the NDMA FP removals (40-80%) by ClO_2 oxidation indicate that reactive amine precursors with pKa values between 7.5 and 9.0 are included in WW effluents used in this study.

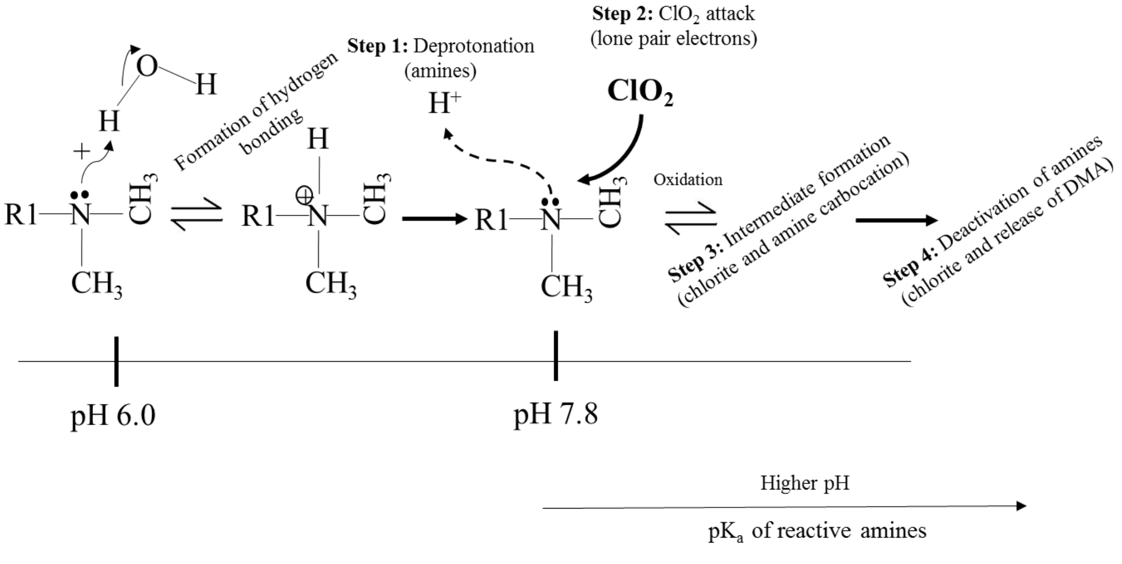


Figure 7.8. Proposed deactivation mechanism of NDMA precursors by ClO_2 oxidation**.**

The Effect of ClO_2 Dose and Ct

The effect of the ClO_2 dose on the NDMA FP removal was investigated at two initial ClO_2 concentrations (i.e., 0.7 and 1.4 mg/L) in TW E, TW D, mixture of 40% TW E + 60 % TW D, and 20% WW-impacted SW O at pH 6.0 and 7.8.

In TW E, at 0.7 mg/L ClO_2 concentration, NDMA FP removals for the initial 10 min oxidation were 10% at pH 6.0 and 28% at pH 7.8, and after 90 min oxidation, they reached 12% at pH 6.0 and 40% at pH 7.8 (**Figure 7.9a**). There was no apparent change in NDMA FP removals from TW D (**Figure 7.10a**) and the mixture of 40% TW E + 60 % TW D with increasing ClO_2 doses from 0.7 mg/L to 1.4 mg/L (**Figure 7.11a**). When 1.4 mg/L of ClO_2 applied, however, NDMA FP removals from only TW E increased significantly at pH 7.8 to 66% (**Figures 7.9b**). NDMA FP removals also increased in 100% TW D and the mixture of TW D & TW E samples with increasing oxidation pH (**Figures 7.10b and 11b**) independent of oxidant dose.

Similar results were observed for 20% WW-impacted SW O at pH 7.8 (**Figure 7.12**), indicating that ClO_2 dose became an important factor at pH 7.8 for the NDMA FP removals from WW-impacted waters (i.e., TW E and 20% WW-impacted SW O). Due to ClO_2 disproportionation, more ClO_2^- and ClO_3^- may form when 1.4 mg/L of ClO_2 is applied. Although ClO_2^- and ClO_3^- do not participate in the deactivation reactions of NDMA precursors, their increased concentrations may change some factors (e.g., ionic strength) influencing electron transfer mechanism to facilitate NDMA FP removals. Since residual ClO_2 (>0.04 mg/L) was always detected even at 0.7 mg/L ClO_2 oxidation, the system was not ClO_2 limited.

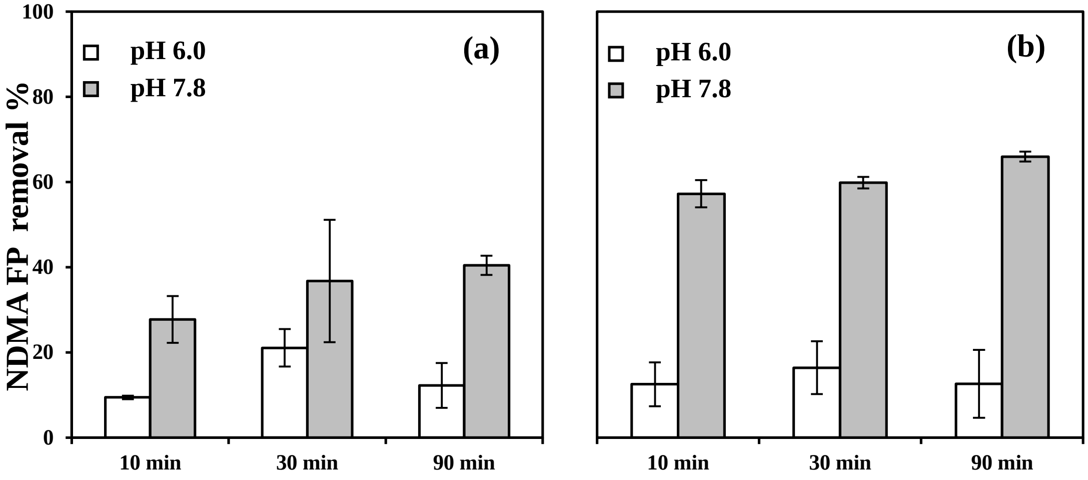


Figure 7.9. Comparison of NDMA FP removals at (a) 0.7 mg/L vs. (b) 1.4 mg/L ClO_2 doses from 100% TW E. Error bars represent data range for duplicate samples.

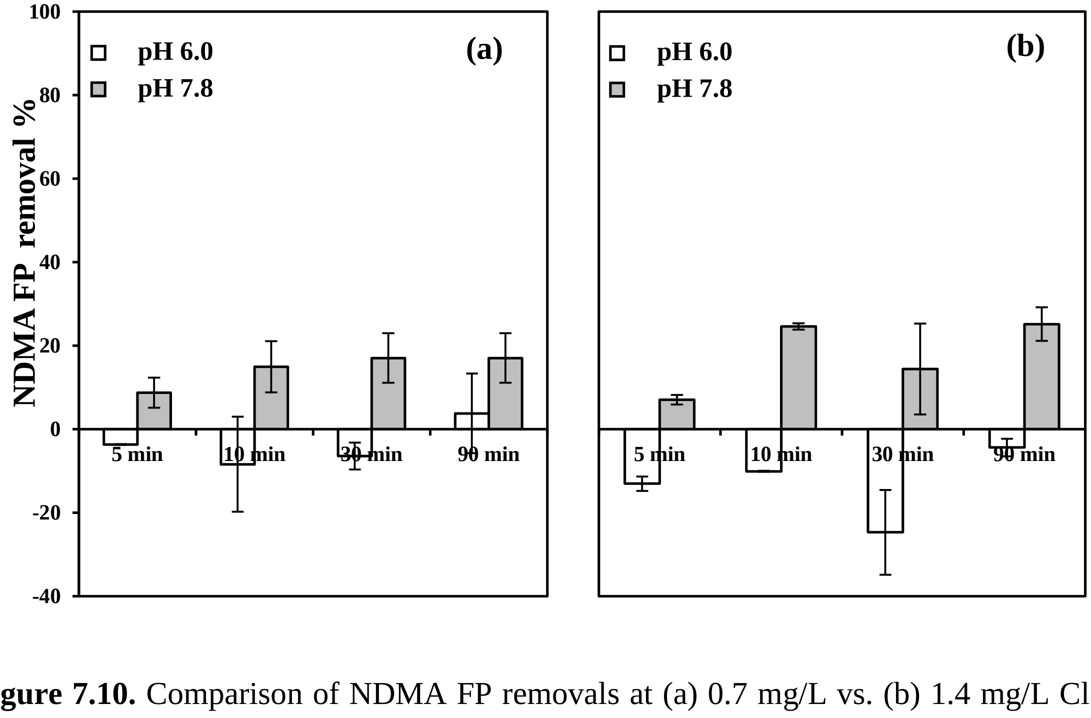


Figure 7.10. Comparison of NDMA FP removals at (a) 0.7 mg/L vs. (b) 1.4 mg/L ClO_2 doses from 100% TW D. Error bars represent data range for duplicate samples.

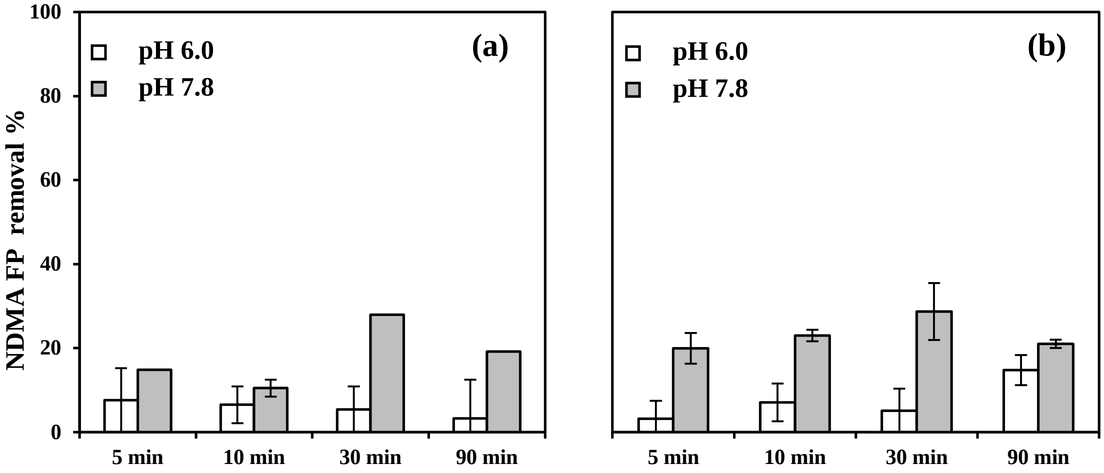


Figure 7.11. Comparison of NDMA FP removals at (a) 0.7 mg/L vs. (b) 1.4 mg/L ClO_2 doses from the mixture of 40% TW E + 60 % TW D. Error bars represent data range for duplicate samples.

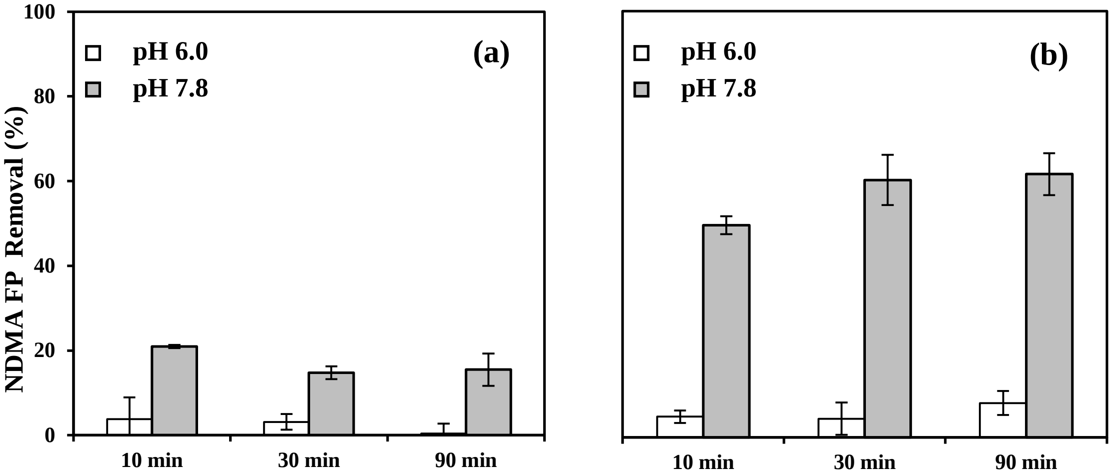


Figure 7.12. Comparison of NDMA FP removals of (a) 0.7 mg/L vs. (b) 1.4 mg/L ClO_2 doses in 20% WW-impacted SW O with EW 2. Error bars represent data range for duplicate samples.

Figure 7.13 shows NDMA FP removals from TW E, TW D, SW I, and 25% impacted SW I as a function of Ct (mg*min/L) values. Presented results indicated that the maximum benefit of ClO_2 oxidation on the NDMA FP removal can be achieved at Ct values less than 10 mg*min/L. Other studies also revealed that low Ct values (<30 mg*min/L) were sufficient to obtain maximum benefits from ClO_2 oxidation (Lee et al., 2007; Sacher et al., 2008; Shah et al., 2012; Selbes et al., 2014). Furthermore, NDMA FP removals were higher at pH 7.8 than pH 6.0, but no further increases were observed at pH 9 (**Figure 7.13b**). This indicates that the maximum benefit of ClO_2 can be achieved even for low Ct values, if the oxidant is applied at high pH (> 7.8) during water treatment.

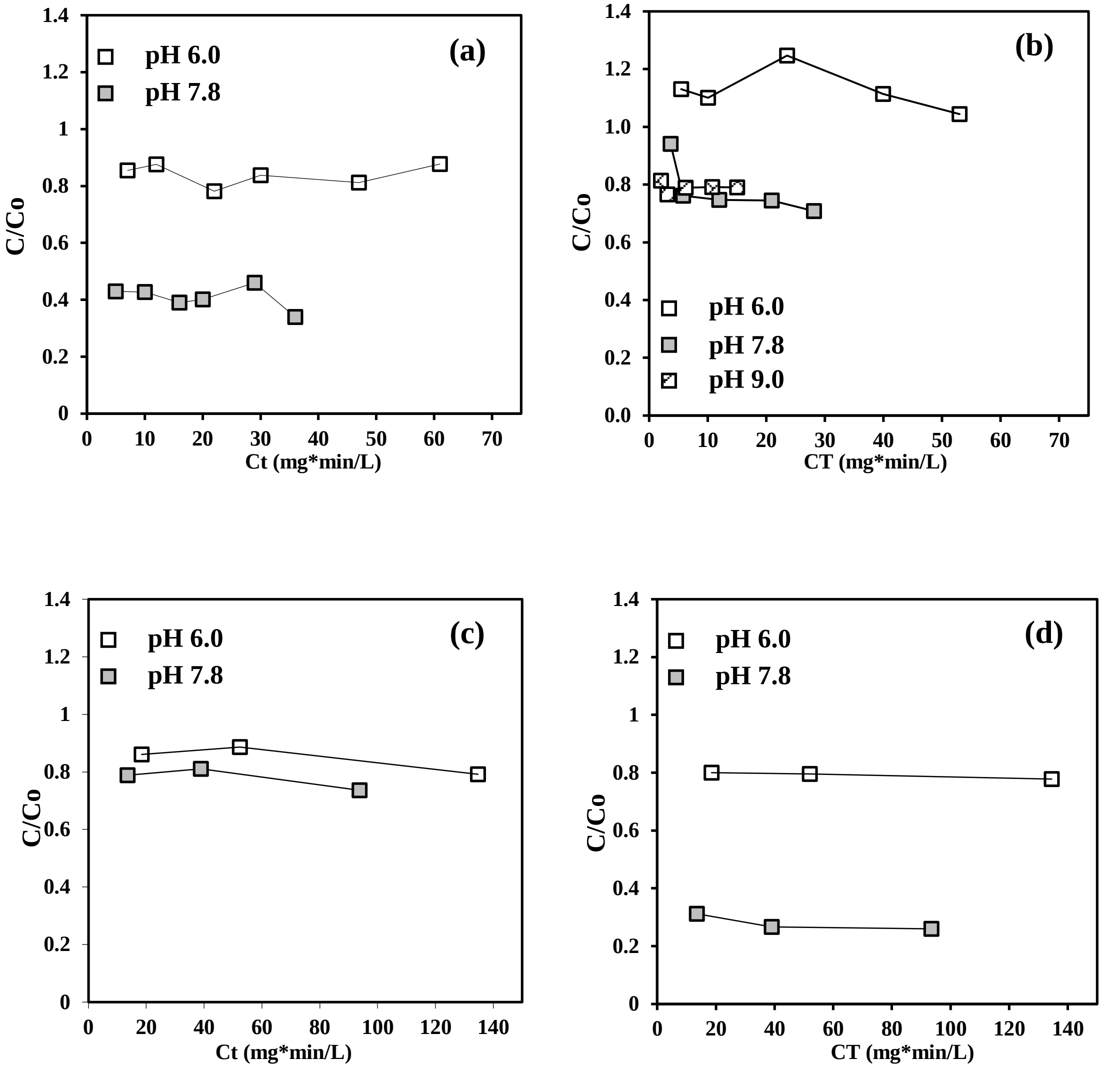


Figure 7.13. ClO_2 effect on NDMA FP removals with respect to Ct values from (a) TW E, (b) TW D, (c) SW I, and (d) 25% WW-impacted SW I.

The Effect of ClO_2 Oxidation on the NDMA Formation under UFC

UFC tests which simulate typical conditions in US distribution systems were also conducted for selected water samples. NDMA formation was investigated in WW-impacted lake waters (i.e., 0%, 10%, 25%, and 50% impacted SW I with EW 1) and WW-impacted SW O (i.e., 0%, 10%, 20%, 50% impacted SW O with EW 2) under UFC conditions (2.7 mg/L pre-formed NH_2Cl for 3 days): (i) without ClO_2oxidation, and (ii) with ClO_2 oxidation (1.4 mg/L) to evaluate the effect of ClO_2 oxidation on the formation of NDMA. Observed NDMA levels under UFC without ClO_2 oxidation (raw) were 3 ng/L, 18 ng/L, 40 ng/L, and 104 ng/L in 0%, 10%, 25%, and 50% WW-impacted SW I waters, respectively (**Figure 7.14**). NDMA levels in WW-impacted SW O waters (0-50%) ranged from 15 to 280 ng/L (**Figure 7.15**). As expected, NDMA formed during UFC tests increased with increasing WW influence.

When ClO_2 (1.4 mg/L) was applied prior to UFC chloramination, NDMA formation in SW I (i.e., non-impacted) was not affected by changes in either oxidation time or pH (**Figure 7.14a**). NDMA formation under UFC varied at pH 6.0 as oxidation time increased and the effect of ClO_2 oxidation was not obvious, while NDMA concentrations in all WW-impacted SW I samples decreased significantly (up to 85%) as a results of oxidation with ClO_2 at pH 7.8 (**Figure 7.14b, c and d**). Similarly, for WW-impacted SW O samples, higher oxidation pH (7.8) resulted in significantly lower NDMA concentrations (**Figure 7.15b, c and d**).

To further examine the pH effect, NDMA formations under UFC were investigated in 20% WW-impacted SW O samples at four pre-oxidation pH (i.e., 6.0, 7.0, 7.8, and 9.0). NDMA formation after 10 min of oxidation decreased by 44%, 62%, 79%, and 78% after 10 min oxidation, and 40%, 58%, 79%, and 81% after 90 min at pH 6.0, 7.0, 7.8, and 9.0, respectively (**Figure 7.16**). NDMA formations decreased with increasing ClO_2 oxidation pH from 6.0 to 7.8, but no additional decrease was observed with further increasing pH. These trends were consistent with the results of FP tests presented before.

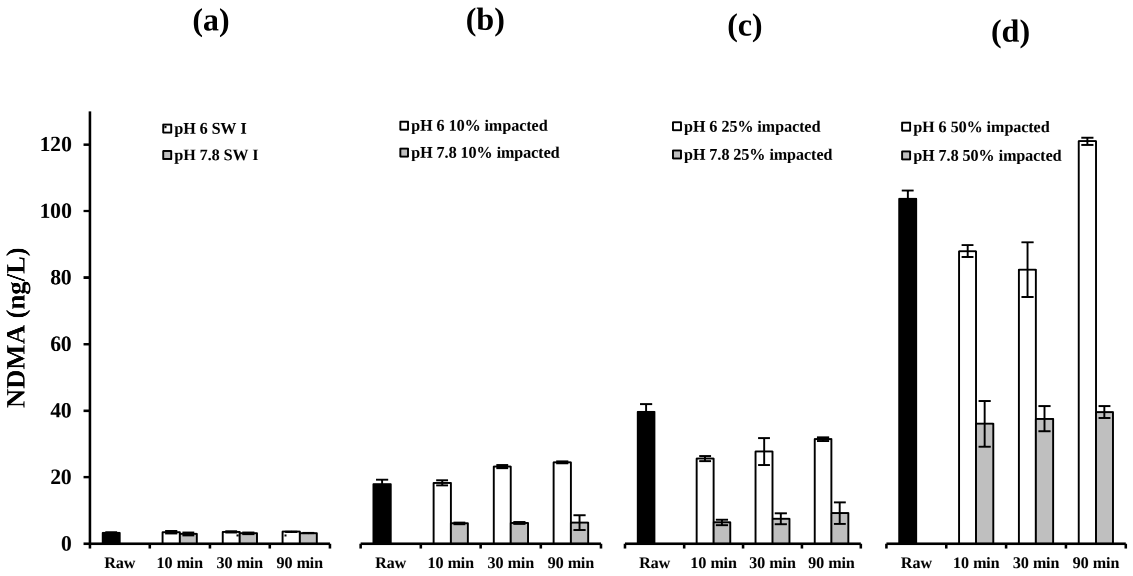


Figure 7.14. Effect of ClO_2 oxidation (pH 6.0 and 7.8) on NDMA formation in (a) SW I, (b) 10% WW-impacted SW I, (c) 25% WW-impacted SW I and (d) 50% WW-impacted SW I. Error bars represent data range for duplicate samples.

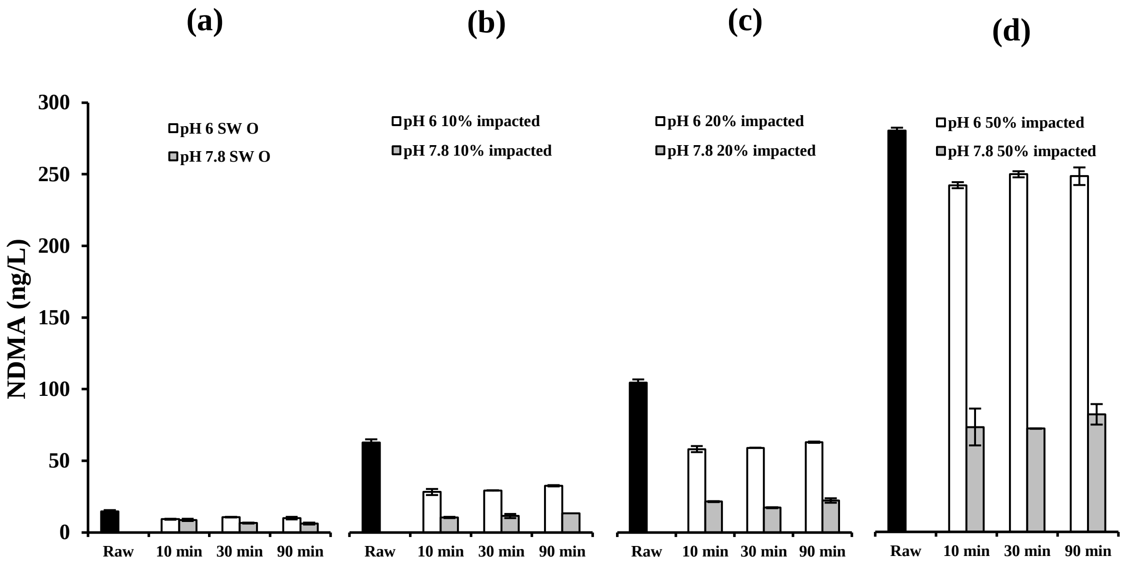


Figure 7.15. Effect of ClO_2 oxidation (pH 6.0 and 7.8) on NDMA formation in (a) SW O, (b) 10% WW-impacted SW O, (c) 20% WW-impacted SW O and (d) 50% WW-impacted SW O. Error bars represent data range for duplicate samples.

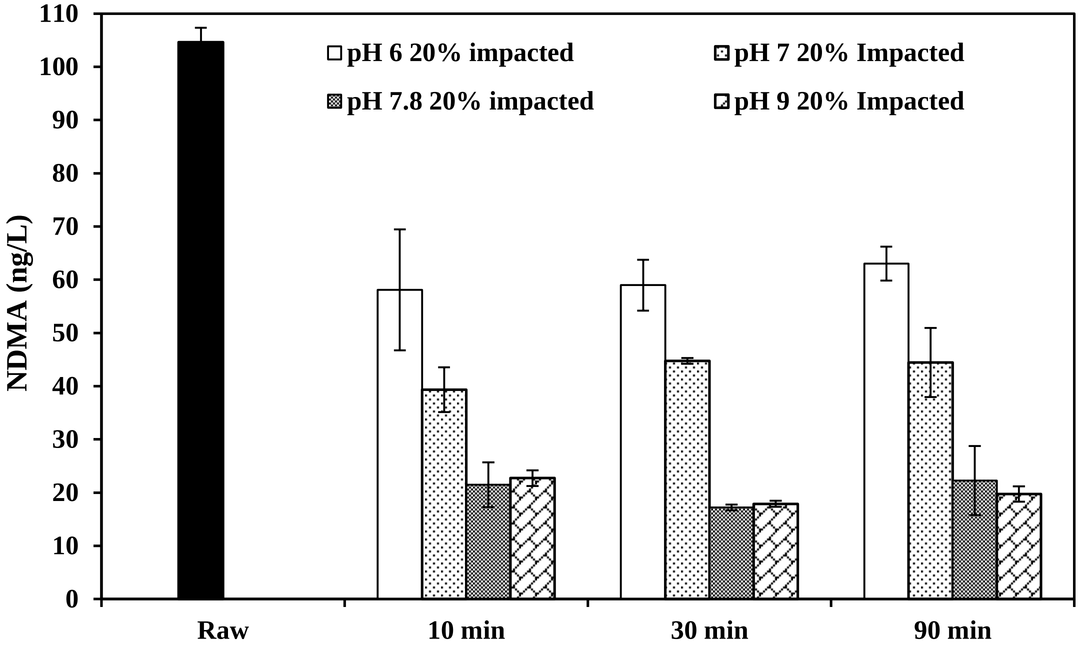


Figure 7.16. NDMA formation change with increasing ClO_2 oxidation pH in 20% WW-impacted SW O. Error bars represent data range for duplicate samples**.**

The Effect of Natural Attenuation on the Reactivity of ClO_2

Previous studies have shown that NDMA FP levels decreased while traveling in the surface waters probably due to natural attenuation processes such as biotic or abiotic degradation, photolysis, and/or sorption reactions (Pehlivanoglu-Mantas and Sedlak 2006; Chen et al., 2009; Krasner et al., 2008; Woods and Dickenson, 2015; Beita-sandi et al., 2016). As a result, the characteristics and reactivity of NDMA precursors may change prior to pre-oxidation with ClO_2.

To evaluate the impact of natural attenuation on the effectiveness of pre-oxidation with ClO_2 on the NDMA FP removal, 25% and 20% WW-impacted waters were prepared by mixing SW I with EW1 and EW2, respectively. Each unfiltered sample was split in two batches. One batch received a stirring bar and was exposed in a glass container under sunlight for 21 days to simulate natural attenuation. The top of the container was covered with aluminum foil to allow air exchange and to prevent the entry of any external components. After 21 days, NDMA FP levels in WW-impacted SW I samples with and without ClO_2 oxidation were measured and compared with those in fresh water samples (t=0 day). For oxidation, ClO_2 was applied at 1.4 mg/L for 90 min prior to chloramination and pH was maintained at 7.8. Without ClO_2 oxidation, NDMA FPs in 25% impacted (EW 1 + SW I) and 20% impacted (EW 2 + SW O) exposed samples decreased by approximately 58% (from 181 ng/L to 75 ng/L) and 68% (from 209 ng/L to 68 ng/L), respectively (**Figure 7.17**). Since exposed samples were not sterilized or filtered and exposed to sunlight, these reactivity decreases can be attributed to combination of attenuation processes (biodegradation, photolysis and sorption).

For 25% EW 1 impacted sample, when ClO_2 was applied, NDMA FP removals were 74% (from 181 ng/L to 47 ng/L) and 69% (from 75 ng/L to 23 ng/L) for fresh (t=0 day) and exposed (t=21 day) samples, respectively, showing similar NDMA FP removals efficiencies (**Figure 7.17a and b**).

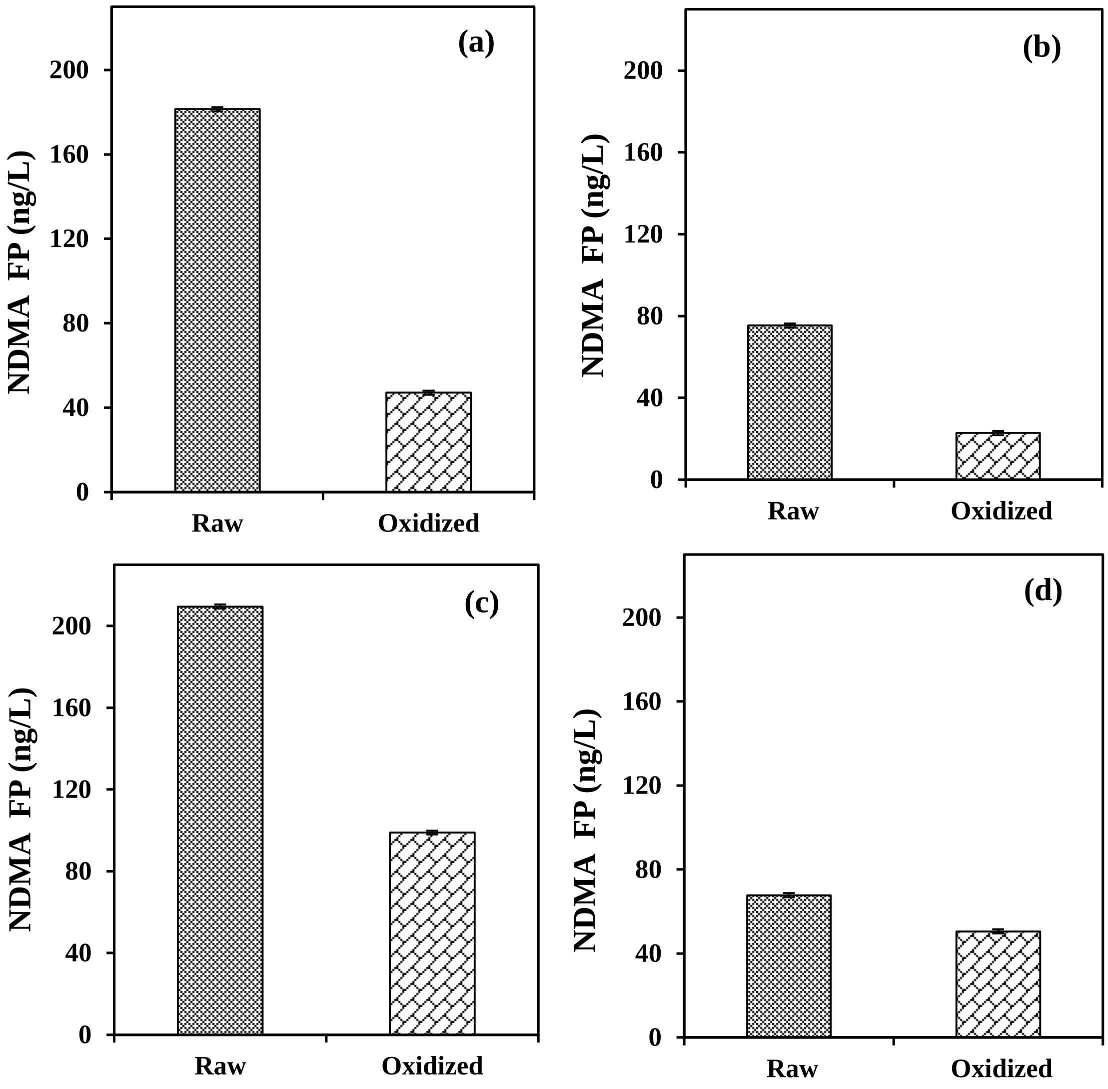


Figure 7.17. NDMA FP levels of raw vs. oxidized waters with ClO_2 in WW-impacted SW I (a) fresh vs. (b) exposed samples, WW-impacted SW D (c) fresh vs. (d) exposed samples. Error bars represent data range for duplicate samples.

For 20% EW 2 impacted sample, however, NDMA FP removals were 53% (from 209 ng/L to 99 ng/L), and 25% (from 68 ng/L to 51 ng/L) for fresh (t=0 day) and exposed samples, respectively (**Figure 7.17c and d**). Lower reactivity towards ClO_2 oxidation found in 20% EW 2 was probably because certain substances present in 20% WW-impacted water may convert to less reactive NDMA precursors as a result of natural attenuation. Since elucidating the loss mechanisms was beyond the scope of this study, I did not further analyze the effect of those natural attenuation processes. Overall, these observations indicate that the reactivity of WW- derived NDMA precursors toward ClO_2 oxidation is water specific as a result of natural attenuation processes. However, observed higher NDMA FP removals (74% and 53%) from fresh (t=0 day) samples indicate that ClO_2 is more effective in the presence of fresh WW-derived NDMA precursors.

THM FP Removal with ClO_2 Pre-oxidation

THM FP tests were also conducted to examine the impact of ClO_2 oxidation on deactivation of THM precursors and to compare with NDMA FP removal results. THM FP removals from TW E and TW D were lower than 21% independent of oxidation conditions (i.e., reaction time and pH) (**Figure 7.18**). **Figure 7.19** shows THM FP removals from SW I and WW- impacted SW I waters at pH 6.0 and 7.8. At both pH, THM FP removals less than 24% regardless of the degree of WW-impact, and slightly more THM FP removals were observed at pH 6.0. Unlike NDMA FP removals, ClO_2 effects on THM FP removals were not significant and pH was not an influencing factor. These observations further support that constituents and properties of NDMA precursors are different from those of THM precursors (Krasner et al., 2015; Uzun et al., 2015).

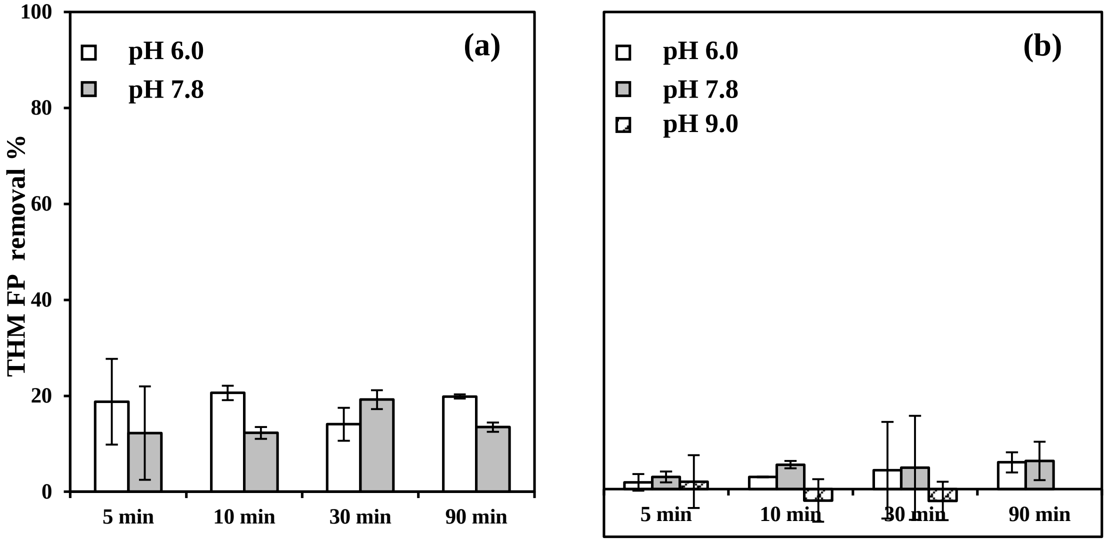


Figure 7.18. THM FP removals from (a) SW E and (b) SW D by ClO_2 oxidation. Error bars represent data range for duplicate samples.

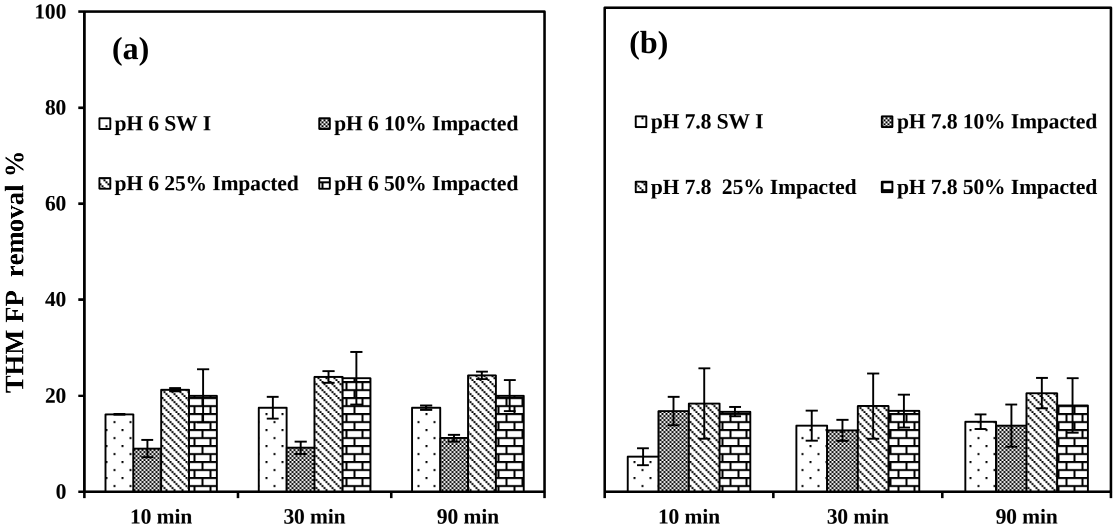


Figure 7.19. THM FP removals in (a) SW I and (b) some degree WW-impacted SW I samples at pH 6.0, and 7.8 with 1.4 mg/L ClO_2. Error bars represent data range for duplicate samples.

Conclusions

ClO_2 oxidation is more effective for reducing NDMA FP in WW-impacted source waters than non-impacted ones, and the percent NDMA FP reduction by ClO_2 significantly increases with increasing WW influence at high pre-oxidation pH (i.e., 7.8). Similarly, a significant decrease is observed in NDMA formation under UFC when the pre-oxidation pH was increased from 6.0 to 7.8 particularly in WW-impacted waters. These observations indicate that oxidation pH is a very critical factor to obtain maximum benefits from ClO_2 oxidation on the control of NDMA formation. Furthermore, the reaction rates of ClO_2 were rapid. Relatively short pre-oxidation periods (i.e., 5-10 min oxidation) or low Ct (~10 mg*min/L) values were sufficient to reach the maximum NDMA FP removals independent of pre-oxidation pH. Increasing ClO_2 dose increased NDMA FP removals from WW-impacted waters only at pH 7.8. ClO_2 dose became an important factor at high pH (> 7.8) conditions in the presence of WW-derived precursors. ClO_2 consumption increases with increasing oxidation pH and DOC levels. Therefore, ClO_2 dose should be optimized based on background DOC values, applied oxidation pH and Ct requirements during water treatment. NDMA FPs in WW-impacted waters decreased after simulated natural attenuation processes, but the reactivity of NDMA precursors were water specific. In a summary, ClO_2 is effective to control NDMA formation in the presence of relatively “fresh” wastewater-derived NDMA precursors when applied at high pH (≥7.8). In contrast, the ClO_2 efficiency on the THM FP removal was low (<24%) and independent of oxidation pH and water type.

CHAPTER EIGHT

REMOVAL OF NDMA FP FROM WASTEWATER- AND POLYMER-IMPACTED WATERS BY INTEGRATED OXIDATION STRATEGIES

Introduction and Objectives

Amines which are potential precursors of NDMA are released from anthropogenic sources such as wastewater treatment plant effluents. It was also shown that municipal wastewater discharges increased from 1980 to 2008 in some of the US surface waters (Rice et al., 2013), which could influence downstream source waters (Uzun et al., 2015).

Another important source of nitrosamine precursors has been known to be amine-based polymers used as coagulants and coagulant aids in water treatment operations (Krasner et al., 2013). A recent survey indicated that 41% of surface water utilities used polymers in treatment operations, with larger systems using them more frequently (USEPA 2009). However, the number may be higher because US polymer suppliers reported that 80% of utilities used polymers as a blend with coagulant, of which they may be unaware (Malcolm Pirnie, 2011). Certain treatment polymers contribute to NDMA formation; these include polyamine, polyDADMAC and polyacrylamide (Kohut and Andrews, 2003; Wilczak et al., 2003; Najm et al., 2004; Park et al., 2007; Park et al., 2009). Decreasing polymer dose, chloramine dose, and chloramine contact time decreased NDMA formation (Wilczak et al., 2003; Mitch and Sedlak 2004; Park et al., 2009). Significant NDMA reductions were observed at some Canadian water treatment facilities when the use of amine-based polymers were discontinued (Andrews and Taguchi, 2000; Najm and Trussell, 2001).

During drinking water treatment, ClO_2 and Cl_2 can be used at different locations for various purposes. To date, either in natural waters or laboratory experiments conducted with model compounds, all the studies focused on the use of oxidants individually. Similarly, two previous studies conducted in DDW background with a single oxidant (Cl_2 or ClO_2) reported opposing results on the deactivation of polymer derived precursors. Selbes and colleagues (2014) prepared solution including polymers, then conducted oxidation experiments with Cl_2 (3.0 mg/L) and ClO_2 (1 mg/L) at pH 7.5. Park et al. (2015) used 10 mg/L oxidants (ClO_2 and Cl_2) and 10 mg/L polymers during pre-oxidation experiments at pH 7.5. Since experiments were conducted in DDW with relatively high oxidation pH conditions, further investigation was needed to examine the effect of different oxidation condition (i.e., oxidation pH and oxidant dose) on deactivating polymer-derived NDMA precursors under realistic water treatment conditions with natural water samples. I presented some positive impact of the simultaneous addition of Cl_2 and ClO_2 in full scale WTPs 3, 4 and 5 (Chapter Six). However, there is no study available investigating the effects of mixed use (i.e., simultaneous or sequential application) of ClO_2 and Cl_2 on the deactivation of NDMA precursors in the literature.

It has been shown that the reaction of $HOCl/OCl^-$ with ClO_2 exhibits complex chemistry (Csordas et al., 2001). There are many intermediates (e.g., $Cl_2O_3^-$, HCl_2O_3, Cl_2O_3, $HClO_2$, Cl_2O_2, Cl^- and etc.) formed during the reaction of ClO_2 with either HOCl or

OCl^-. **Figure 8.1** illustrates major products formed during the reaction of ClO_2 with $HOCl/OCl^-$.

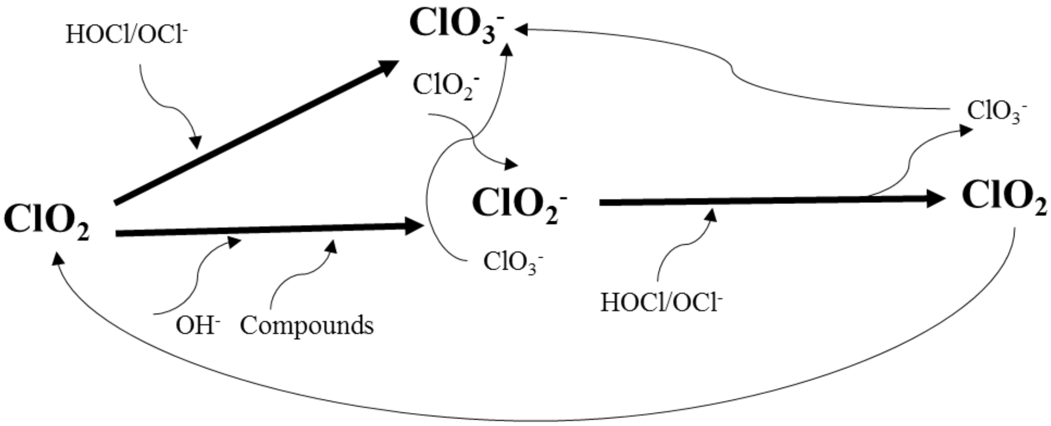


Figure 8.1. ClO_2 decomposition and redox reaction in the presence of $HOCl/OCl^-$.

Although ClO_2 disproportionates to ClO_2^- and chlorate (ClO_3^-) ions under alkaline conditions, it is stable under acidic conditions (Csordas et al. 2001). However, in the presence of HOCl or OCl^- direct redox reaction occurs with ClO_2 and HOCl/OCl are being consumed (Equations 8.1 and 8.2) (Csordas et al. 2001). ClO_3^- is usually the final product for the reaction of ClO_2 with chlorine species, however, the fate of ClO_2 depends on the stoichiometric ratio of the reactants (Kormanyos et al. 2008).

$HOCl + 2ClO_2 + H_2O == 2ClO_3^- + Cl^- + 3H^+$ **Equation 8.1**

$OCl^- + 2ClO_2 + H_2O == 2ClO_3^- + Cl^- + 2H^+$ **Equation 8.2**

In terms of the reaction rates, ClO_2 is oxidized more quickly by OCl^- than HOCl, and the ClO_2/OCl^- is not associated with any change in the rate law as a function of pH (Csordas et al. 2001). Furthermore, the reaction of HOCl and ClO_2^- formed ClO_2 (Csordas et al.

2001). Due to the reaction of HOCl with ClO_2^-, the presence of HOCl is expected to decrease ultimate ClO_2^- formation compared to ClO_2 only in natural waters. These reactions cause the reformation of ClO_2 during the dynamic complex reactions by oxychlorine species.

Considering the possible effect of ClO_2 oxidation on model compounds and direct redox reaction of ClO_2 and HOCl/OCl^-, I hypothesized that integrated oxidation with ClO_2 and Cl_2 might be more beneficial in two ways: i) intermediates or radicals (e.g., $Cl_2O_3^-$, HCl_2O_3, Cl_2O_3, $HClO_2$, Cl_2O_2, and etc.) that are formed during the reaction of HOCl/OCl^- with ClO_2 can involve deactivation process of NDMA precursors, and ii) HOCl can deactivate reactive intermediates such as DMA released from the reaction of ClO_2 with NDMA precursors.

Thus, the main objectives in this phase of the study were to investigate i) the effects of individual, simultaneous, and sequential applications of ClO_2 and Cl_2 on the removal of NDMA FPs from different source waters (e.g., non-impacted vs. either WW or polymer impacted waters), and ii) the effects of oxidation pH and oxidant dose. Due to regulatory significance, the formation of THMs, ClO_2^- and ClO_3^- were also monitored for selected experiments.

Water Samples

Wastewater-impacted Water Samples

Non-impacted surface water (SW I) and two municipal WWTP effluent water samples (EW 1 and 2) were collected and used to prepare two 20% WW-impacted samples

(IW 1 and 2) by mixing treated effluent waters (EW 1 and 2, respectively) with SW I. Polymer-impacted water samples (0.25 mg/L polyamine, 0.5 mg/L polyDADMAC, and 2.0 mg/L polyacrylamide), to simulate some polymer applications during water treatment, were also prepared by spiking a pre-determined amount of polymer stock solutions into the SW I samples. **Table 8.1** shows the selected water quality parameters of the water samples used in oxidation experiments.

Table 8.1. Selected water quality parameters for the lake and wastewater impacted water samples**.**

Water type	Sample name	DOC (mg/L)	$SUVA_{254}$ (L/mg-min)	Bromide (μg/L)	DON (mg/L)	NDMA FP (ng/L)
Lake water	SW I	3.1	2.1	<MRL	0.1	55
WWTP 1 effluent Water	EW 1	4.4	1.6	41	2.5	980
EW 1 impacted water	IW 1	3.3	1.7	15	0.6	238
WWTP 1 effluent Water	EW 2	9.7	1.5	87	10.0	1115
EW 2 impacted water	IW 2	4.1	1.8	27	2.1	259

MRL= Minimum reporting level.

Polymer-impacted Water Samples

To prepare polymer-impacted natural water samples, 500 mg/L (as active ingredients) of polymer stock solutions were prepared for each polymer in DDW and used in further dilutions. Three different polymers were tested in this study: polyamine (37.66% by weight) and polyDADMAC (20% by weight) purchased from Scientific Polymer and Sigma Aldrich, respectively, and Sedifloc 400C polyacrylamide polymer (powder) obtained from WTP 5. The polymer doses were selected to yield a target NDMA FP levels of 200-350 ng/L in natural water samples to evaluate the effectiveness of oxidation strategies.

Pre-oxidation Experiments

The upper limit for the initial dose of ClO_2 was set at 1.4 mg/L to keep ClO_2^- formation under the regulatory limit (1.0 mg/L) while the upper limit of free chlorine was set at 2.2 mg/L to minimize the formation of regulated DBPs. Initial doses of 0.7 and 1.1 mg/L for ClO_2 and Cl_2, respectively, were also applied to selected samples to investigate the effect of oxidant dose on the deactivation of NDMA precursors and formation of other DBPs (i.e., THM, ClO_2^- and ClO_3^-). Two oxidant contact times (i.e., 10 and 60 min) and two oxidation pH conditions (i.e., 6.0 and 7.8) were tested during the experiments. All experiments were conducted in 1000 mL amber glass bottles at room temperature (21-23 ^oC).

Figure 8.2 shows the details of the pre-oxidation strategies used in this study. Five different oxidation scenarios were tested (i) individual oxidant applications (scenario 1: ClO_2 only, scenario 2: Cl_2 only), (ii) simultaneous oxidant (scenario 3: ClO_2 and Cl_2) application (**Figure 8.2a**), and (iii) sequential applications, (scenario 4: ClO_2 first and then Cl_2, scenario 5: Cl_2 first and then ClO_2) (**Figure 8.2b**). In this study, either simultaneous or sequential application of oxidants were termed integrated oxidation.

Residuals of ClO_2 and/or Cl_2 after pre-determined contact times (i.e., 10 and 60 min) were measured using a HACH DR/820 colorimeter with DPD colorimetric test kits. For the residual chlorine measurements in the integrated oxidation samples, 40 ml of samples were taken from each bottle and residual ClO_2 was removed by purging with nitrogen gas (5 min). FP tests were conducted to determine the maximum levels of precursors of NDMA and THM in a sample after 5 days of reaction time in the presence of excess amounts of NH_2Cl and Cl_2, respectively. Pre-determined volumes of NH_2Cl stock solution and Cl_2 stock solution (5-6% available free Cl_2) were spiked to achieve initial doses of 100 mg/L of NH_2Cl and 50 mg/L initial Cl_2 for NDMA FP and THM FP tests, respectively. After 5 days contact time at room temperature, residual oxidants were measured and quenched with sodium thiosulfate and sodium sulfite, respectively, before extractions.

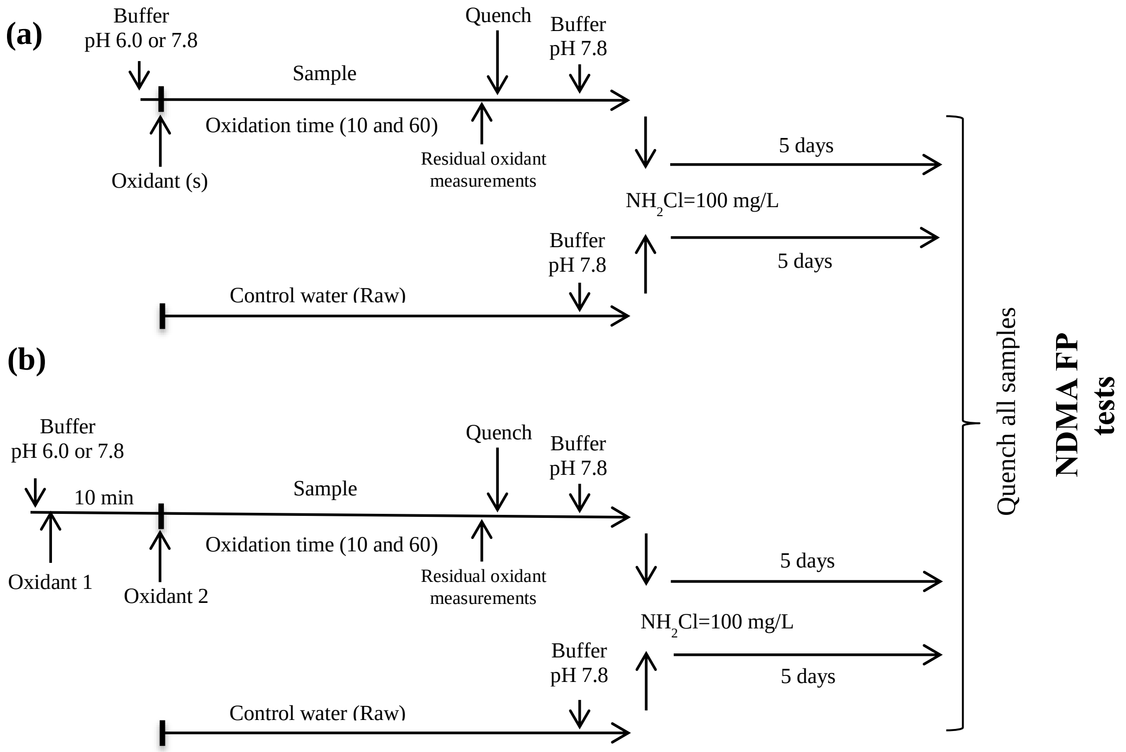


Figure 8.2. Experimental matrix for pre-oxidation strategies for (a) individual and simultaneous and (b) sequential oxidant applications.

In addition to FP tests, for selected samples, UFC test were also conducted with 3.0 mg/L initial dose of chloramine for three days at pH 7.8 (**Figure 8.3**). After pre-oxidations (i.e., 10 and 60 min) (i.e., pH 6.0 and 7.8), no quenching agent was added to UFC samples prior to chloramination. Instead, residual chlorine concentrations were adjusted to 3.0 mg/L and then a pre-determined amount of ammonium sulfate solution was spiked immediately to form chloramines corresponding to a 4:1 chlorine-to-ammonia ratio by weight.

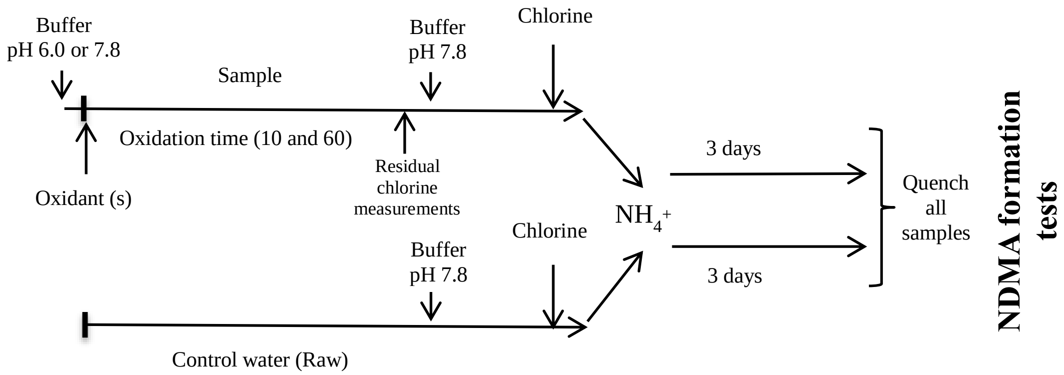


Figure 8.3. UFC tests procedure after simultaneous and sequential application of oxidants.

Samples were stored in the dark for three days, extracted, and analyzed for NDMA. The NDMA FP and UFC tests were also conducted without any pre-oxidation with the raw water samples as a control. Due to regulatory and practical significance, THMs, ClO_2^-, and ClO_3^- were also monitored for selected samples (**Figure 8.4**). After pre-oxidation (60 min), 80 ml (40 ml for THMs and 40 ml for ClO_2^- and ClO_3^- measurements) of samples were taken from each bottle. For THM formation tests, residual oxidants were quenched with a stoichiometric amount of sodium sulfite and/or sodium thiosulfate. For ClO_2^- and ClO_3^- measurements, residual ClO_2 was removed by purging with nitrogen gas (5 min). Then, 50 mg/L ethylenediamine (EDA) preservative solution was added into the samples. After addition of either preservative solution or quenching agents, samples were kept in the refrigerator until analysis. For the ClO_2^- and ClO_3^- analysis, samples were prepared and analyzed using an ion-exchange chromatography (Dionex ICS-2100) equipped with an anion separation column (Dionex AS23) and guard column (Dionex AG23) according to USEPA Method 300.1 Part B. Chemical standards, analytical methods used for NDMA, THMs and other water quality measurements are described in Chapter Four. All analytical methods and minimum reporting level (MRLs) are summarized in **Table 4.2.**

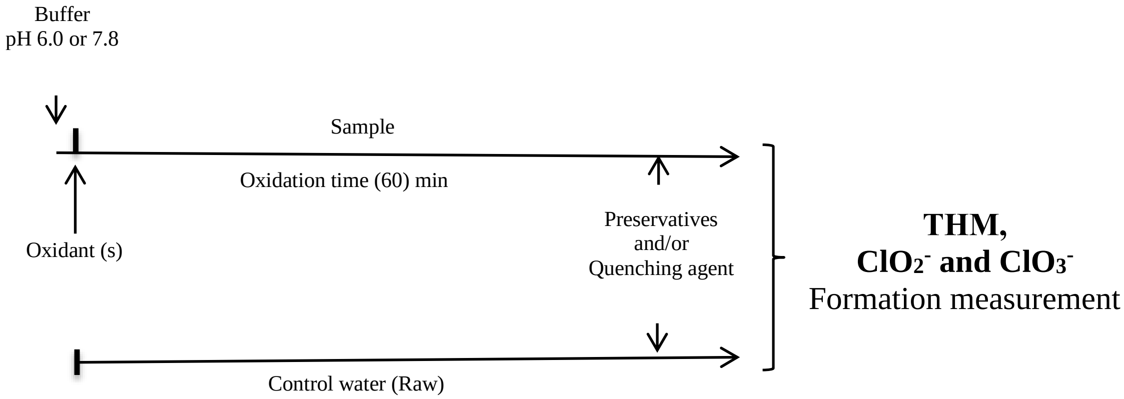


Figure 8.4. Measurements of THMs, ClO_2^- and ClO_3^- for oxidation experiments before chloramination.

Results and Discussions

Effect of Oxidation Strategies: In Wastewater-impacted Waters

Lake water sample yielded 55 ng/L NDMA FP which represents the base line for comparison with the pre-oxidation experiments (**Table 8.1**). NDMA FP removals as a result of different oxidation scenarios are shown in **Figure 8.5**.

Results showed that the deactivation of NDMA precursors in the lake water tested was low with respect to both ClO_2 and/or Cl_2 oxidation. Scenario 1 (only ClO_2) exhibited negative removal of NDMA FPs regardless of oxidant doses at pH 6.0. However, at pH 7.8 removals of 14% and 8% were observed for 1.4 and 0.7 mg/L doses, respectively.

As indicated before, the pre-oxidation pH was important in the removal of NDMA FP by ClO_2. Contact times longer than 10 min did not affect the NDMA FP removals. On the other hand, NDMA FP removals were between -3 and 18% for pre-oxidation with Cl_2 only, and simultaneous and sequential applications of ClO_2 and Cl_2 (i.e., scenarios 2, 3, 4 and 5). No obvious trend was observed in terms of oxidation pH and oxidant doses.

These results showed that the deactivation of NDMA precursors in the lake water tested was low (<20%) with respect to both ClO_2 and/or Cl_2 oxidation. This low removal allowed use of the lake water as a background water to investigate the effect of oxidation strategies on the removal of NDMA FPs in both WW- or polymer-impacted waters. Therefore, the NDMA FP of two WW-impacted samples (80% from SW I + 20% from effluent waters) prepared in the laboratory, IW 1 and IW 2, without pre-oxidation were 238 and 259 ng/L, respectively (**Table 8.1**), and these values were used to calculate the effect of oxidation strategies on the NDMA FP removals.

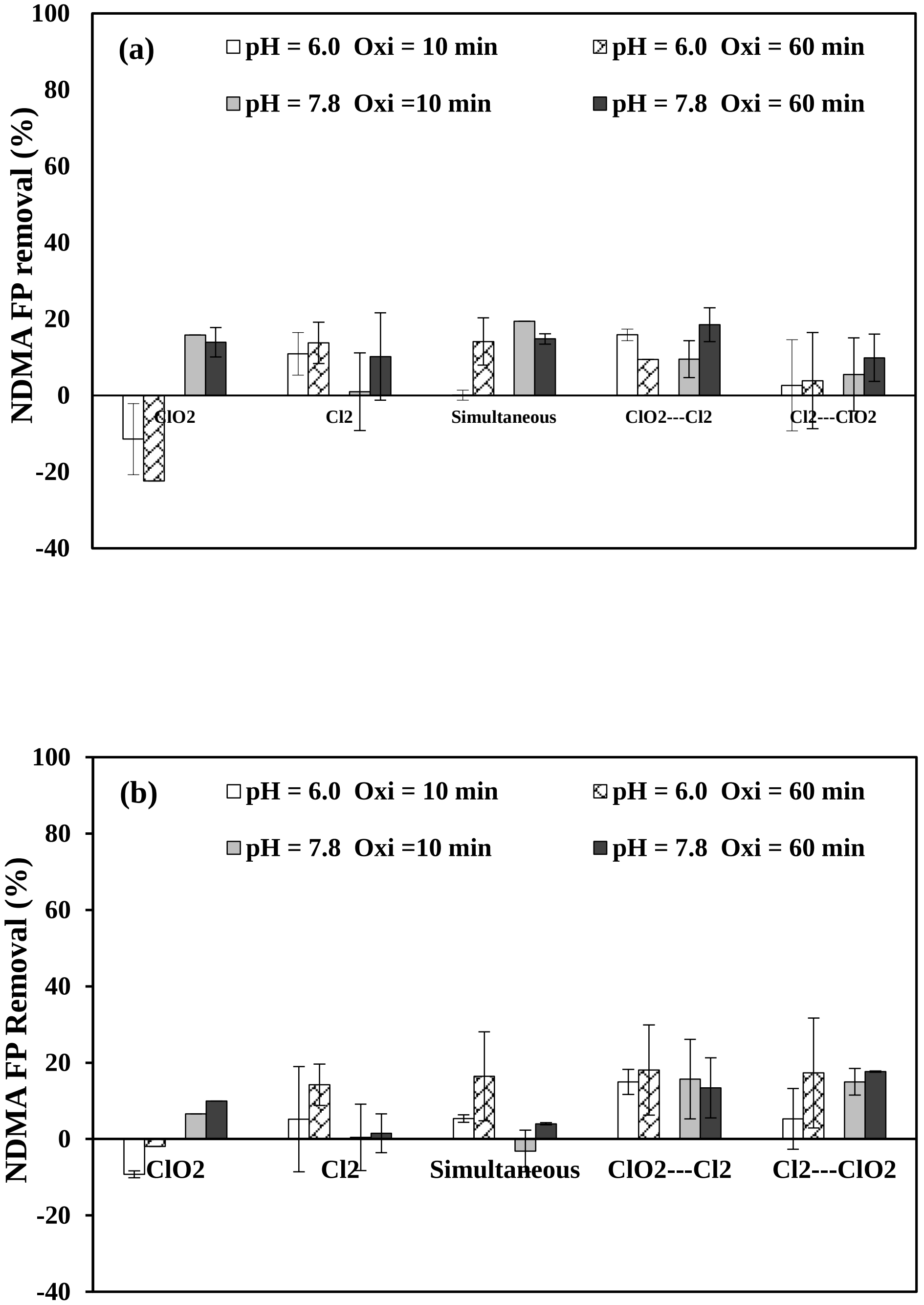


Figure 8.5. Effect of pre-oxidation strategies on the removal of NDMA FP in lake water samples with (a) 1.1 mg/L ClO_2 and/or 2.2 mg/L Cl_2 and (b) 0.7 mg/L ClO_2 and/or 1.1 mg/L Cl_2. Error bars represent data range for duplicate samples.

Scenario 1 (pre-oxidation with ClO_2 only): Pre-oxidation with ClO_2 at the higher dose (1.4 mg/L, **Figure 8.6a**) achieved higher removals of NDMA FP at both pH levels for IW 1 than the lower dose (0.7 mg/L, **Figure 8.7a**). Similarly, NDMA FP removals for IW 2 were 2-13% at pH 6.0 and 63-73% at pH 7.8 with 1.4 mg/L of ClO_2 (**Figure 8.6b**). However, the NDMA FPs increased (-11%) at pH 6.0, while 16-32% of NDMA FP removals were observed at pH 7.8 (**Figure 8.7b**). Although, IW 1 and IW 2 had comparable water quality levels (**Table 8.1**) NDMA FP from IW 1 was, in general, ~10% lower compared to IW 2. However, significantly higher NDMA FP removals by ClO_2 oxidation were achieved at higher oxidation pH (i.e., 7.8) in both waters.

Increasing the ClO_2 dose also played a positive role at high pH (i.e. 7.8) in both waters (IW 1 and IW2). These results confirm that relatively “fresh” WW-impacted water has reactive precursors that can be deactivated (up to 75%) by ClO_2. High removal efficiencies can be associated with i) higher reaction rates of ClO_2 with amines at higher oxidation pH (Lee et al., 2007; von Gunten and Ramseier, 2010; Gates et al., 2009), and ii) the presence of highly reactive amines that have higher NDMA molar yields (>3%) with relatively higher pKa values (>7.5) in the WW effluent waters. NDMA FP levels from certain amine precursors with relatively high pKa (>7.5) (e.g., ranitidine, benzyl amine, 3-dimethylaminobenzene, and etc.) with high NDMA yields during chloramination decreased drastically after pre-oxidization with ClO_2 (Lee et al., 2007; Selbes et al., 2014). Due to the oxidation reactions with ClO_2, precursors may be broken into small fragments such as DMA. If the parent compound has higher molar yield of NDMA than DMA (<3%), the overall NDMA FP removals is expected to decrease. Otherwise, the overall NDMA FP removals will increase after pre-oxidation with ClO_2.

Scenario 2 (pre-oxidation with Cl_2 only): When 2.2 mg/L of Cl_2 was applied for pre-oxidation, NDMA FP removals from IW 1 were 41% at pH 6.0 and 55% at pH 7.8 after either 10 or 60 min of reaction times (**Figure 8.6a**). However, the removals decreased about 10% at both pH 6.0 and 7.8 for 1.1 mg/L of Cl_2 application (**Figure 8.7a**). NDMA FP removals from IW 2 were 28-43% at pH 6.0 and 32-56% at pH 7.8 with 2.2 mg/L of Cl_2 (**Figure 8.6b**), while 1.1 mg/L of Cl_2 achieved only 12% of removals at both pH 6.0 and 7.8 (**Figure 8.7b**). Since the DOC value (4.1. mg/L) of IW 2 was higher than the other tested waters (**Table 8.1**), measured free chlorine residuals after oxidation were low (0.50-0.73 and 0.10-0.18 mg/L for 2.2 mg/L and 1.1 mg/L initial doses of Cl_2 for 60 min of oxidation times, respectively).

Thus, low NDMA FP removals by low dose (initial dose of 1.1. mg/L) of Cl_2 might be attributed to competition of background organic materials with NDMA precursors for chlorine. With 2.2 mg/L of Cl_2, NDMA FP removals from both IW 1 and IW 2 were improved about 4-17% at higher pH. This was consistent with previous findings which indicated the importance of oxidation pH and the presence of deprotonated amines during oxidation with free chlorine (Lee and von Gunten, 2010; Krasner et al., 2013; Selbes et al., 2014).

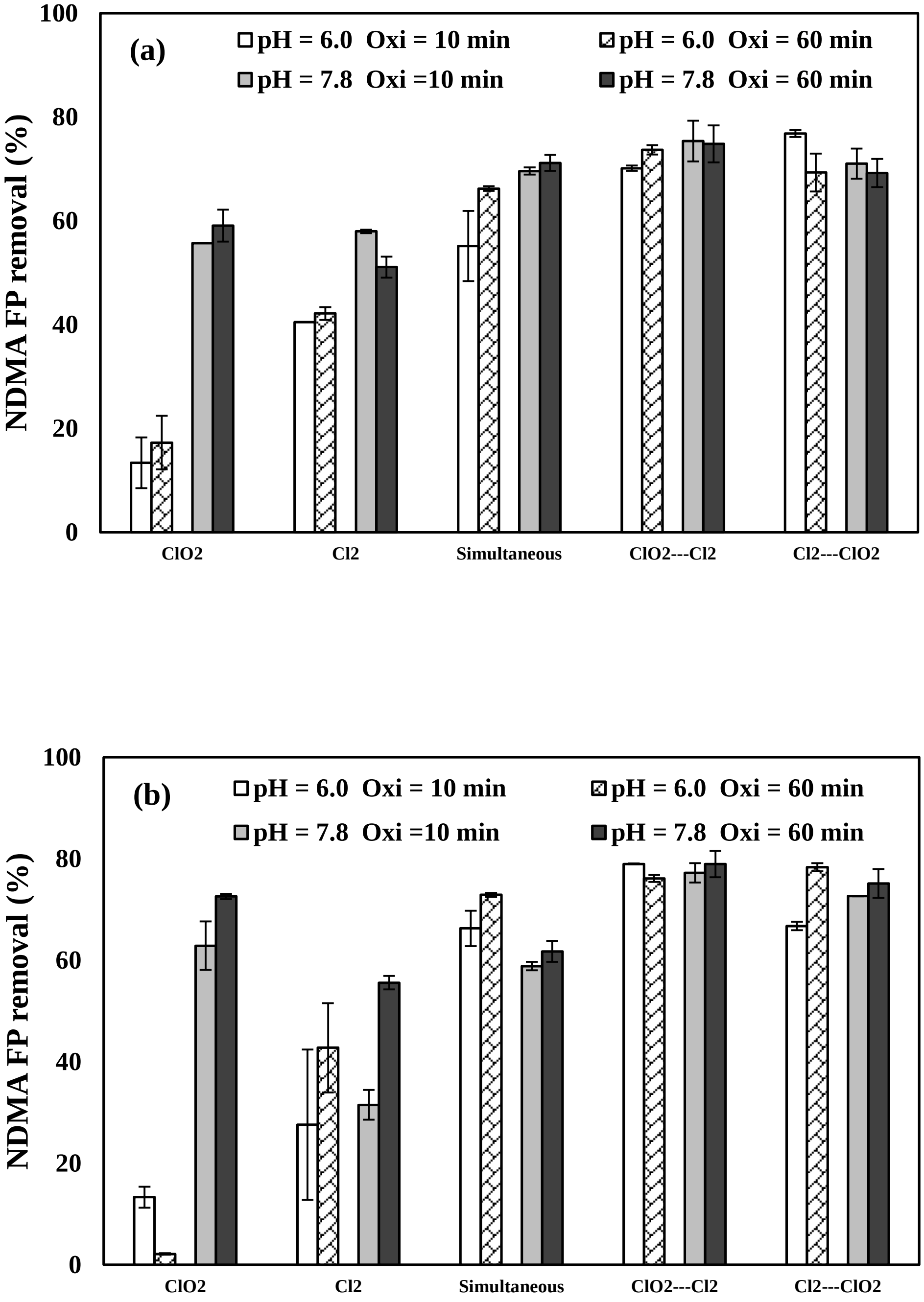


Figure 8.6. Effect of pre-oxidation strategies on the removal of NDMA FP from (a) IW 1 and (b) IW 2 for 1.4 mg/L of ClO_2 and/or 2.2 mg/L of Cl_2. Error bars represent data range for duplicate samples.

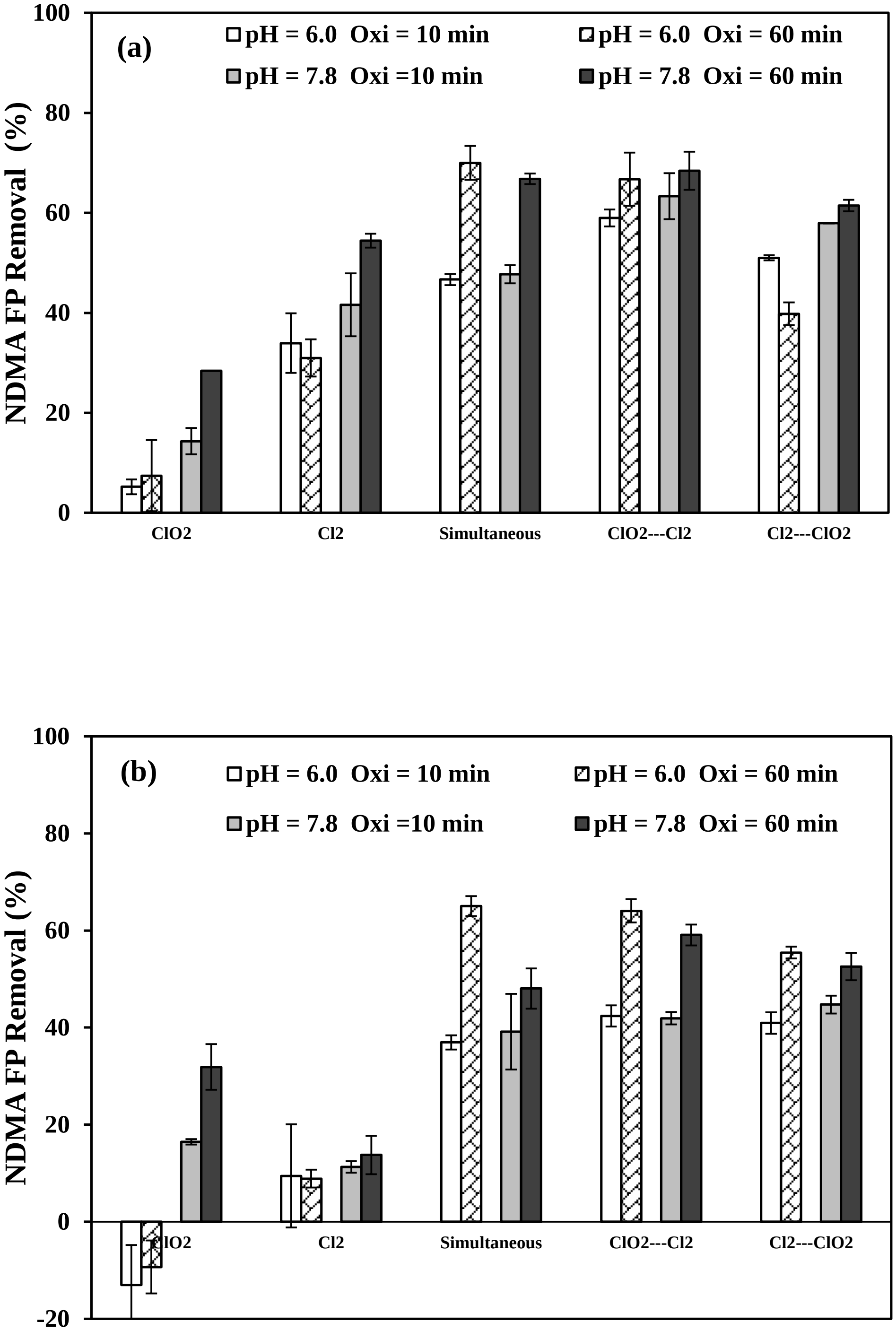


Figure 8.7. Effect of pre-oxidation strategies on the removal of NDMA FP from (a) IW 1 and (b) IW 2 for 0.7 mg/L of ClO_2 and/or 1.1 mg/L of Cl_2. Error bars represent data range for duplicate samples.

Scenarios 3, 4, and 5 (simultaneous or sequential addition of Cl_2 and ClO_2): For the removal of NDMA FP from WW-impacted waters, either simultaneous or sequential application of ClO_2 and Cl_2 was more effective than individual oxidation at pH 6.0 and 7.8 (**Figures 8.6 and 8.7**). For higher doses (1.4 mg/L of ClO_2 and 2.2 mg/L of Cl_2), 3-4 times more NDMA FP removals in IW 1 were observed at pH 6.0 compared to ClO_2 only while increases in the NDMA FP removals by either simultaneous or sequential application were just 3-26% at pH 7.8. However, compared to Cl_2 only, increases in the NDMA FP removals by simultaneous or sequential application were 50-80% at pH 6.0 and 29-36% at pH 7.8 (**Figure 8.6a**). When relatively high doses of oxidants were used, oxidation time between 10 min and 60 min did not play an important role in NDMA FP removals (**Figure 8.6a**). For low doses of ClO_2 and Cl_2, however, NMDA FP removals increased with oxidation time (**Figure 8.7a**) indicating that 1.4 mg/L of ClO_2 and 2.2 mg/L of Cl_2 are sufficient doses to deactivate NDMA precursors present in the studied waters within 10 min. This suggests that both oxidation pH and reaction time can be influential factors for low dose of oxidant application conditions depending on background organic levels in water.

In IW 2, in general, similar NDMA FP removal trends were observed. NDMA FP removals significantly increased at pH 6.0, when both high and low doses of oxidants were applied. Unexpectedly, NDMA FP removals (59-62 %) from IW 2 by scenario 3 (ClO_2 and Cl_2) did not exceed the NDMA FP removals achieved (63-73%) by the application of ClO_2 alone at pH 7.8 (**Figure 8.6b**). However, for scenarios 4, and 5 NDMA FP removals (73-79 %) were slightly higher compared to scenarios 1, 2, and even 3. Application of higher oxidant doses (ClO_2=1.4 mg/L and Cl_2=2.2. mg/L) ensured higher removal of NDMA FP in both oxidation pH conditions (i.e., 6.0 and 7.8) from two different WW-impacted waters in this study.

Integrated oxidation strategies resulted in more drastic changes in the NDMA FP removals compared to individual oxidant applications at pH 6.0 than pH 7.8. It indicates that the ClO_2 works better at relatively high pH for deactivating amine precursors with high pKa values. NDMA FP removals by integrated oxidation (either simultaneous or sequential) were always higher than the sum of those achieved by the use of individual oxidants (i.e., ClO_2 only and Cl_2 only) at pH 6.0. This might be due to the following reasons: i) selective reactivity of certain precursors toward Cl_2 or ClO_2, ii) additional deactivation of precursors by intermediates formed during the reaction of Cl_2 with ClO_2, and iii) further Cl_2 deactivation of reactive products such as DMA released from the reaction of ClO_2 with amine precursors. In contrast to the case at pH 6.0, NDMA FP removals by integrated oxidation at pH 7.8 were lower than the sum of those achieved by individual oxidants when high dose (1.4 mg/L of ClO_2 and 2.2 mg/L of Cl_2) applied (**Figure 8.6**). This is related to higher reaction of either Cl_2 or ClO_2 with amines at higher pH (von Gunten et al., 2010; Selbes et al., 2014). Since the reaction of amine precursors with individual oxidants increase at higher pH, those transformed to more reactive forms toward both oxidants (Cl_2 and ClO_2). Therefore, NDMA FP removals for integrated oxidations were lower than the sum of those achieved by individual oxidants. However, NDMA FP removals by integrated application of oxidants were comparable with sum of those achieved by individual oxidants for the low dose (0.7 mg/L of ClO_2 and 1.1 mg/L of

Cl_2) (**Figure 8.7**). This, again, suggests that background organic level in the water can be an influential factor for deactivation of NDMA precursors when sufficient oxidants were not applied.

Overall, these observations suggest that the use of integrated oxidation (ClO_2 and Cl_2) can be an effective strategy for deactivating NDMA precursors present in source waters under the influence of WW effluents. Some practical options to consider are i) simultaneous use of ClO_2 and Cl_2 during conventional clarification at pH 6.0, ii) oxidation with ClO_2 only (>1 mg/L) around pH 8.0, iii) integrated use of ClO_2 and Cl_2 after increasing pH to about 8.0. The latter two conditions may be used as post-oxidation (e.g., in clearwells for Ct credit).

Effect of Oxidation Strategies: In Polymer-impacted Waters

NDMA FP removals by pre-oxidation strategies were also investigated with polymer impacted waters. Polyamine, polyDADMAC and polyacrylamide were added into the lake water at the doses of 0.25, 0.5, and 2.0 mg/L, respectively. Without pre-oxidation, NDMA FPs of polyamine (0.25 mg/L), polyDADMAC (0.5 mg/L), and polyacrylamide (2.0 mg/L) containing samples were 291, 239, and 334 ng/L, respectively. Polymer-impacted waters were treated with single (i.e., scenarios 1 and 2) or integrated oxidation (i.e., scenarios 3, 4 and 5) for high oxidant dose (ClO_2=1.4 mg/L and Cl_2=2.2 mg/L) applications. For low dose oxidation (ClO_2=0.7 mg/L and Cl_2=1.1 mg/L) condition, only scenarios 1, 2, and 3 were tested.

Polyamine-impacted water: Previously studies were conducted in DDW with relatively high oxidation pH conditions compared to typical conventional treatment conditions (natural water background about pH ~6.0) (Selbes et al., 2014; Park et al., 2015). Therefore, further investigation was needed to examine the effect of oxidations on polymer-derived NDMA precursors under realistic water treatment conditions with natural water samples. Integrated oxidation strategies were also needed to better understand deactivation of NDMA precursors in polymer-impacted waters. In this study, for pre-oxidation with ClO_2 (i.e., scenario 1) or Cl_2 (i.e., scenario 2) alone, NDMA FP removals from polyamine-impacted waters ranged 24-40% and 23-49%, respectively, independent of oxidation pH and oxidant dose (**Figure 8.8a and 8.9a**). However, previously two studies reported opposing results on the deactivation of polyamine precursors with free chlorine or chlorine dioxide pre-oxidation (Selbes et al., 2014; Park et al., 2015). Both of these studies were conducted in distilled and DDW background. Selbes et al. (2014) prepared solutions including 0.2 mg/L polyamine, then oxidation experiments were conducted with Cl_2 (3.0 mg/L) and ClO_2 (1 mg/L) at pH 7.5. They found that the polyamine-derived NDMA precursors were not deactivated by either ClO_2 or Cl_2. On the other hand, Park et al. (2015) used 10 mg/L oxidants (ClO_2 and Cl_2) and 10 mg/L polymers during pre-oxidation experiments at pH 7.5. They reported that the removal of NDMA FP reached up to 30% with ClO_2 and 80% with Cl_2 treatment. As indicated in the study these removals might be associated with structural change of polyamine-derived precursors as a result of oxidation (Park et al., 2015).

For a simultaneous (i.e., scenarios 3) or sequential application (i.e., scenarios 4 and 5) of ClO_2 and Cl_2, 8-29% higher NDMA FP removals were observed at both pH 6.0 and 7.8 compared to individual oxidation scenarios (i.e., scenarios 1 and 2). The order of oxidant addition (i.e., simultaneous, ClO_2 first, or Cl_2 first) did not exhibit a major influence on the overall NDMA FP removals when 1.4 mg/L of ClO_2 and 2.2 mg/L of Cl_2 were applied. However, scenario 4 (ClO_2 first and then Cl_2) showed slightly better NDMA FP removals. This might be related to the further deactivation of reaction products such as DMA released (Park et al., 2015) from the reaction of ClO_2 with polyamine-derived precursors in the presence of Cl_2. Overall, integrated use of ClO_2 and Cl_2 for pre-oxidation achieved more than 50% of polyamine-derived NDMA FP removal independent of reaction time and oxidation pH. Furthermore, higher oxidant doses (ClO_2=1.4 mg/L and Cl_2=2.2. mg/L) ensured better removal of NDMA FP in both oxidation pH conditions (i.e., 6.0 and 7.8).

PolyDADMAC-impacted water: The overall removals of NDMA FP from polyDADMAC-impacted waters were 11-17% for pre-oxidation with ClO_2 and 35-42% for pre-chlorination (**Figure 8.8b),** with a high dose (1.4 mg/L of ClO_2 and 2.2 mg/L) of oxidants. NDMA FP removals were independent of oxidation pH and reaction time. Oxidant dose and integrated use of oxidants were found to be important factors for deactivation of polyDADMAC-derived precursors. Although the experimental conditions were different from previous studies, these NDMA FP removal trends were similar to those found in the literature (Park et al., 2015; Selbes et al., 2014). Furthermore, for high oxidant doses, simultaneous (scenarios 3) applications of ClO_2 and Cl_2 resulted in similar removals compared to the use of Cl_2 alone (scenarios 2), while sequential applications of ClO_2 and Cl_2 (scenarios 4 and 5) resulted in 11-22% more removals at pH 6.0 and 7.8 (**Figure 8.8b**). This indicates that the deactivation ability of Cl_2 is similar to that of ClO_2 for polyDADMAC-derived precursors, and reactive intermediates released from the reaction of ClO_2 and HOCl/OCl^- may participate in further deactivating poly DADMAC-derived precursors when sufficient oxidants were used. On the other side, lower oxidant dose (0.7 mg/L of ClO_2 and 1.1 mg/L of Cl_2) resulted in lower removals (~7-48%) under the scenarios 2 and 3 (**Figure 8.9b**). These findings suggest that Cl_2 is better than ClO_2 for deactivation of polyDADMAC–derived precursors, and integrated oxidations can accomplish more than 40% removal of polyDADMAC-derived NDMA FP independent of the reaction time and oxidation pH. Sufficient oxidant dose applications is required to attain maximum benefit.

Polyacrylamide-impacted water: For polyacrylamide containing waters, pre-oxidation with 1.4 mg/L ClO_2 (i.e., scenario 1) resulted in 10-20% NDMA FP removals, while pre-oxidation with 2.2 mg/L Cl_2 (i.e., scenario 2) increased NDMA FPs (**Figure 8.8c**). With 1.1 mg/L Cl_2, higher NDMA FP removals were achieved at pH 7.8 than 6.0 (**Figure 8.9c**). Simultaneous (scenarios 3) and sequential applications of 1.4 mg/L ClO_2 and 2.2 mg/L Cl_2 (scenarios 4 and 5) at pH 6.0 and 7.8 resulted in about 30% NDMA FP removals which were greater than those by a single oxidant uses (i.e., ClO_2 or Cl_2 alone), whereas simultaneous applications of 0.7 mg/L ClO_2 and 1.1 mg/L Cl_2 did not show any beneficial effects on deactivation of polyacrylamide-derived precursors compared to single oxidant uses.

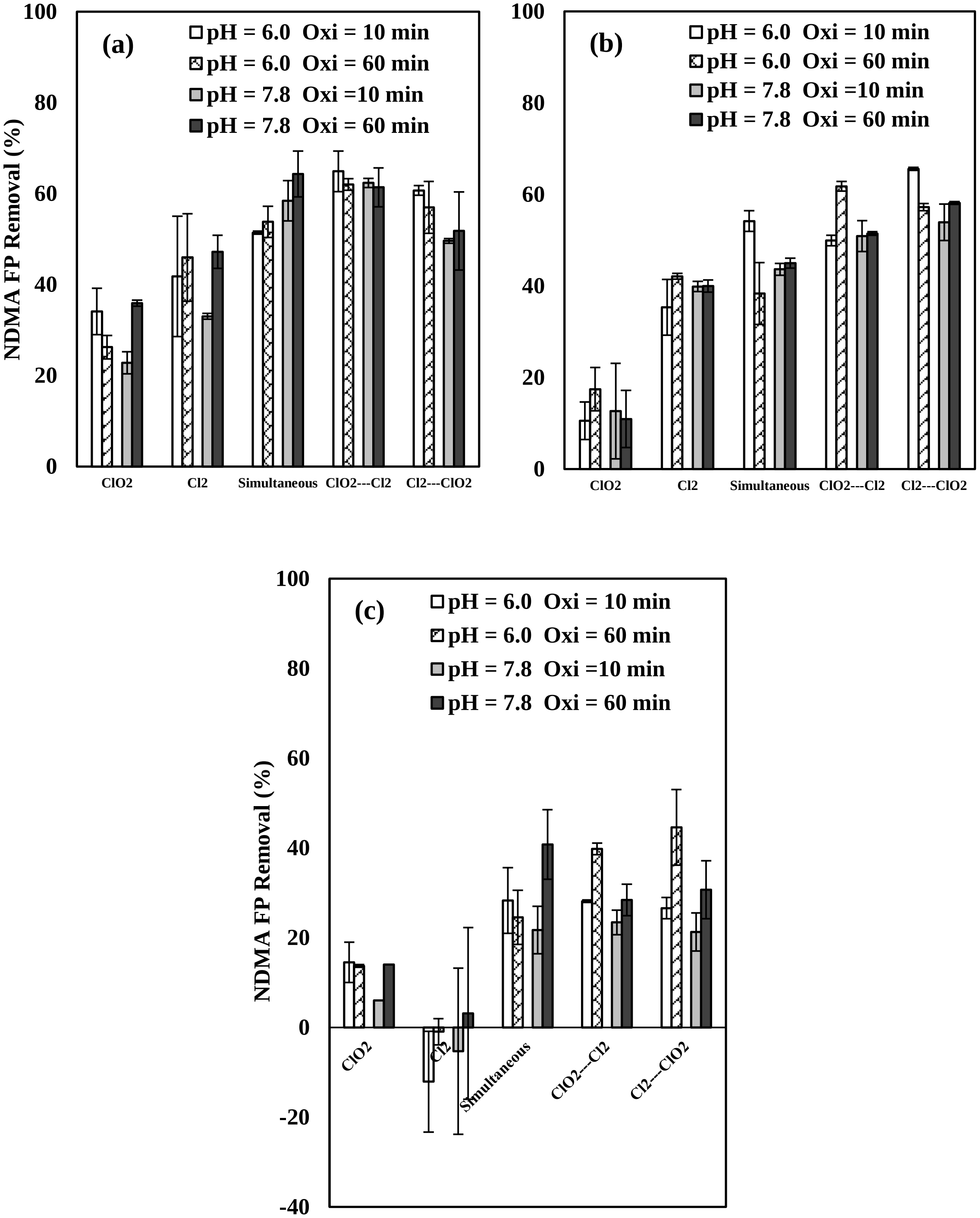


Figure 8.8. Effect of pre-oxidation strategies on the removal of NDMA FP from (a) polyamine (0.25 mg/L) (b) polyDADMAC (0.5 mg/L) and (c) polyacrylamide (2 mg/L) impacted lake water samples for 1.4 mg/L of ClO_2 and/or 2.2 mg/L of Cl_2. Error bars represent data range for duplicate samples.

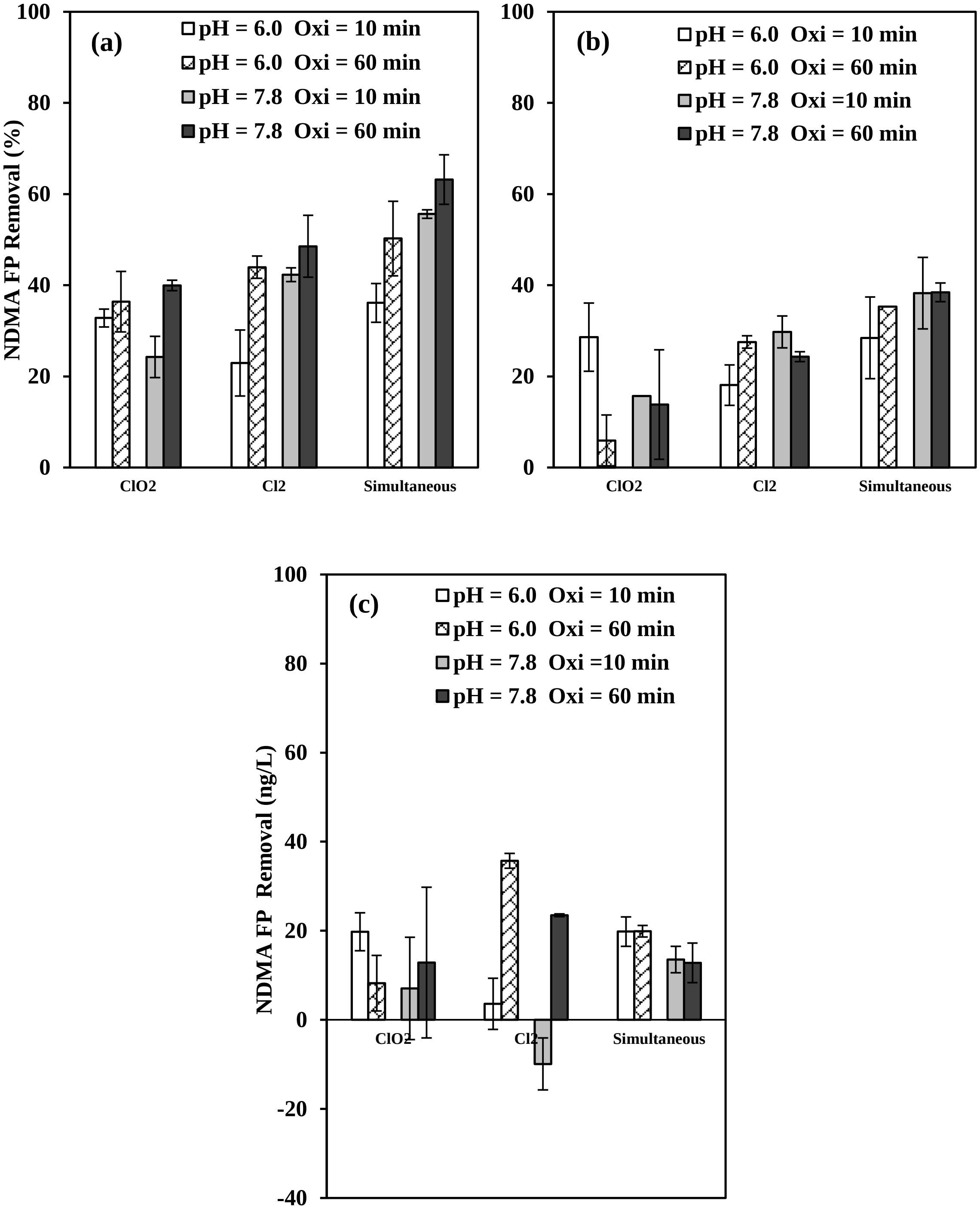


Figure 8.9. Effect of selected pre-oxidation strategies on the removal of NDMA FP from (a) polyamine (0.25 mg/L) (b) polyDADMAC (0.5 mg/L) and (c) polyacrylamide (2 mg/L) impacted lake water samples for 0.7 mg/L of ClO_2 and/or 1.1 mg/L of Cl_2. Error bars represent data range for duplicate samples.

This suggests that oxidant doses are more important factors than pH or oxidation time for the control of polyacrylamide-derived precursors. **Table 8.2** summarizes the results obtained for the NDMA FP removals from polymer-impacted waters by individual and integrated oxidation with ClO_2 and Cl_2. In general, polymer-derived precursors were better deactivated by simultaneous or sequential addition of Cl_2 and ClO_2 than by the use of single oxidants. In order to obtain the maximum benefits for deactivating precursors, sufficient oxidant doses (e.g., 1.4 mg/L ClO_2 and 2.2 mg/L Cl_2) were required.

Table 8.2. NDMA FP removals in polymer impacted natural waters.

	Oxidants dose	ClO_2 only	Cl_2 only	Simultaneous or Sequential	Notes
Polyamine-impacted water	High[a] Dose	23-36%	33-46%	50-64%	○ Integrated use of ClO_2 and Cl_2 for pre-oxidation achieved more than 50% of polyamine-derived NDMA FP removal, independent of the reaction time and oxidation pH. ○ Higher oxidant doses ensured better removal of NDMA FP in both oxidation pH conditions (i.e., 6.0 and 7.8).
	Low[b] Dose	24-36%	23-49%	36-63%	
PolyDADMAC-impacted water	High Dose	11-17%	35-42%	38-66%	○ Pre-oxidation strategies except only ClO_2 application can accomplish more than 40% removal of polyDADMAC-derived NDMA FP independent of the reaction time and oxidation pH. ○ High oxidant dose applications required to attain maximum benefit.
	Low Dose	6-29%	18-30%	28-38%	
Polyacrylamide-impacted water	High Dose	6-15%	(-12)-3%	21-45%	○ Integrated applications of oxidants at pH 6.0 and 7.8 resulted in about 30% NDMA FP removals which are greater than those by single oxidant uses. ○ High oxidant dose applications required to attain maximum benefit.
	Low Dose	8-20%	(-10)-36%	13-20%	

[a] Initial dose of ClO_2 = 1.4 mg/L and Cl_2 = 2.2 mg/L.
[b] Initial dose of ClO_2 = 0.7 mg/L and Cl_2 = 1.1 mg/L.

Effect of Oxidation Strategies: UFC Results

To simulate typical US distribution systems, NDMA formations in selected waters were also examined under UFC conditions (i.e., oxidized with 3.0 mg/L initial dose of chloramines for 72 hr at pH 7.8). NDMA formations were investigated in IW 1 (i.e., 20% EW 1 + 80% lake water) and 0.5 mg/L polyDADMAC containing lake water. NDMA levels without pre-oxidation under UFC were 51 ng/L in IW I and 27 ng/L in polyDADMAC containing lake water, corresponding to 21% and 11%, respectively, of the measured NDMA FPs in the same waters.

Wastewater-impacted Water (IW 1): NDMA formations in IW 1 under UFC decreased by about 20% with 1.4 mg/L ClO_2 or 2.2 mg/L Cl_2 at pH 6.0 and about 90% at pH 7.8 (**Figure 8.10a**). Both oxidants, ClO_2 and Cl_2, were effective for deactivation of WW-derived precursors with increasing pH. NDMA formation in IW 1 was suppressed by simultaneous applications of ClO_2 and Cl_2 independent of pH. When 0.7 mg/L ClO_2 and 1.1 mg/L Cl_2 were applied, NDMA formation increased by <10% at pH 6.0 and <30% at pH 7.8 (**Figure 8.10b**) indicating that oxidant doses were also important for the control of WW-derived NDMA precursors. These findings indicate that pre-oxidation pH is a critical factor for the control of WW-derived NDMA precursors, and increasing oxidation pH increases deactivation of NDMA precursors when ClO_2 or Cl_2 are applied. The trends observed from the UFC tests were also consistent with those of FP tests (**Figure 8.6a**). Simultaneous application of ClO_2 and Cl_2 achieved less NDMA formation than using single oxidants. Also, this benefit to control NDMA formation from WW-impacted waters was more significant when higher oxidants were applied (ClO_2=1.4 mg/L and Cl_2= 2.2 mg/L) independent of oxidation pH.

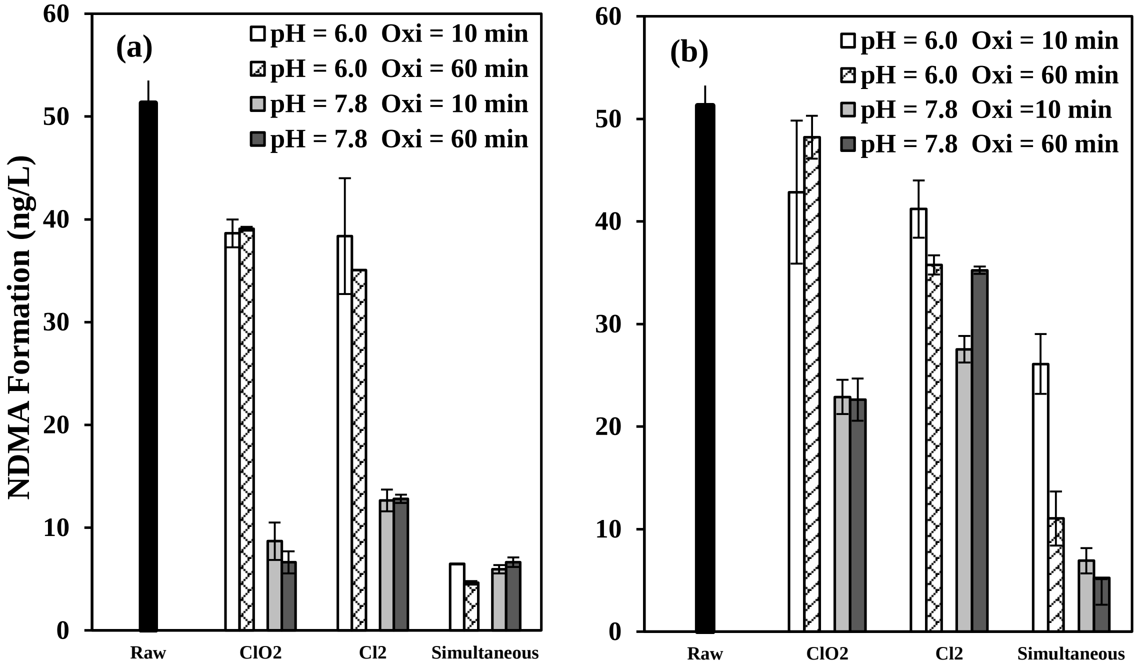


Figure 8.10. Effect of selected pre-oxidation strategies on the formation of NDMA from IW 1 under UFC for (a) 1.4 mg/L of ClO_2 and/or 2.2 mg/L of Cl_2 and (b) 0.7 mg/L of ClO_2 and/or 1.1 mg/L of Cl_2. Error bars represent data range for duplicate samples.

PolyDADMAC-impacted water: Unlike WW-impacted waters, individual or simultaneous oxidation with ClO_2 and Cl_2 did not lead to considerable decreases in the NDMA formation in polyDADMAC containing water under UFC (**Figure 8.11**). Changes in either oxidation pH or oxidant dose did not influence the formation of NDMA. According to the FP test results, integrated oxidation showed more NDMA FP removals than the use of single oxidants (**Figure 8.11**). Although the pH effect was not apparent, increasing oxidant doses achieved increases in the NDMA FP removals from polyDADMAC-impacted waters.

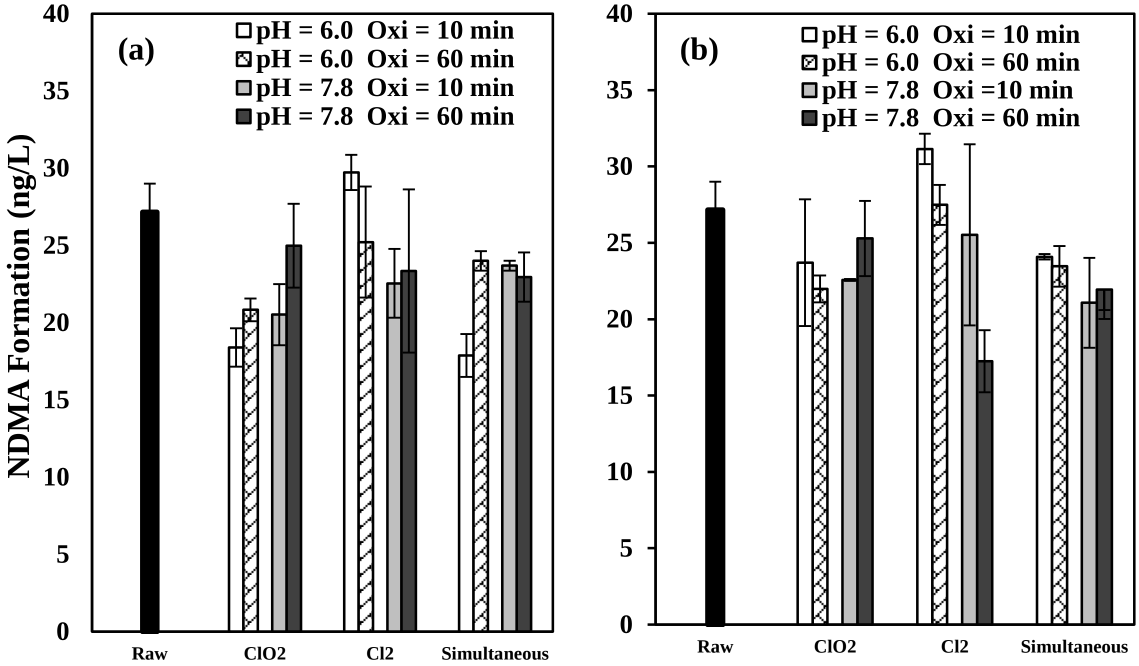


Figure 8.11. Effect of selected pre-oxidation strategies on the formation of NDMA from polyDADMAC impacted (0.5 mg/L) lake water for (a) 1.4 mg/L of ClO_2 and/or 2.2 mg/L of Cl_2 and (b) 0.7 mg/L of ClO_2 and/or 1.1 mg/L of Cl_2. Error bars represent data range for duplicate samples.

However, under UFC none of the oxidation methods tested resulted in significant benefits for the control of NDMA formation. In this study, the UFC test yielded only 27 ng/L NDMA, while the FP test with the same water sample (0.25 mg/L polyDADMAC in lake water) produced about 239 ng/L of NDMA. This difference might be caused by different $NHCl_2$ concentration levels in two chloramination methods. During the FP test, >1.5 mg/L of residual $NHCl_2$ was always detected due to decomposition of NH_2Cl, and this level of $NHCl_2$ is much greater than the residual $NHCl_2$ (<0.05 mg/L) found during the UFC test because of different initial preformed chloramine concentration (100 mg/L for the FP test vs. 3 mg/L for the UFC test). It has been reported that the presence of $NHCl_2$ resulted in more NDMA formation from polyDADMAC-derived precursors (Park et al.

2015). Therefore, different removal efficiencies by ClO_2 and Cl_2 oxidation for FP and UFC tests is mainly because of the characteristics of precursor reactivity. In other words, most polyDADMAC-derived precursors are more sensitive to NH_2Cl, thus less presence of $NHCl_2$ leads to lower deactivation of precursors.

Effect of Oxidation Strategies: Other DBPs

THMs and ClO_2^- which are currently regulated DBPs, and ClO_3^- were also measured after pre-oxidation in lake water and WW-impacted water 1 (IW 1) for the purpose of comparison. Bromide levels in the tested waters were ≤15µg/L. When ClO_2 alone was applied for pre-oxidation, almost no THMs formed (**Figure 8.12**) in both waters. When high dose (2.2 mg/L) of Cl_2 alone was applied to lake water for pre-oxidation, 14-25 µg/L of THMs formed and THM formation increased with increasing pH (**Figure 8.12**). Simultaneous or sequential (especially ClO_2 first and then Cl_2) additions of oxidants decreased THM formation by 60% compared to Cl_2 alone. However, THM formation for scenario 5 (Cl_2 first and then ClO_2) was similar to that for pre-chlorination indicating that the reactions between THM precursors and Cl_2 occur before ClO_2 is added (**Figure 8.12**). The formation of ClO_2^- and ClO_3^- depended on the applied ClO_2 doses and pH. When 1.4 mg/L ClO_2 alone was applied, 475-570 µg/L of ClO_2^- and 50-65 µg/L ClO_3^- formed. As ClO_2 dose decreased to 0.7 mg/L, the formation of ClO_2^- and ClO_3^- also decreased. The formation of ClO_2^- and ClO_3^- increased with increasing pH because decomposition of ClO_2 is favored under basic conditions (**Figure 8.12**). On the other hand, when Cl_2 was applied simultaneously or sequentially with ClO_2, ClO_3^- formations increased significantly at both pH 6.0 and 7.8. These increases in ClO_3^- can be attributed to the reaction of HOCl with

ClO_2. Furthermore, addition of Cl_2 decreased the formation of ClO_2^-, especially, when high dose of oxidants (1.4 mg/L Cl_2 and 2.2 mg/L Cl_2) were applied compared to oxidation with ClO_2 alone. This is attributed to the reaction of HOCl with ClO_2^-. Similar DBP formation trends were observed in WW-impacted water (IW 1) (**Figure 8.13).**

Overall, these observations showed that the formation of THM and ClO_2^- was reduced with simultaneous or sequential (only for ClO_2 first then Cl_2) oxidation, while ClO_3^- formation increased.

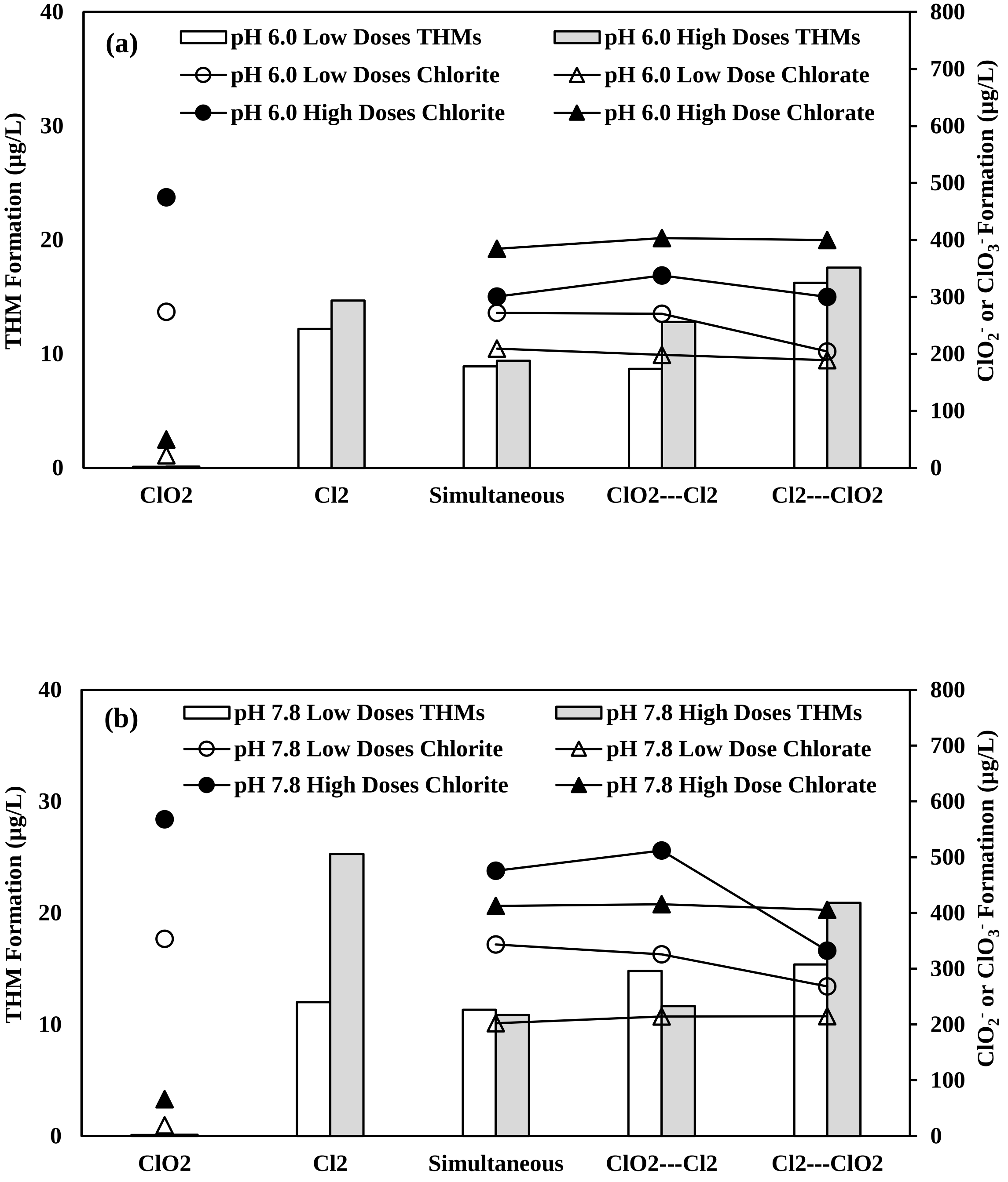


Figure 8.12. The effect of individual and oxidation strategies on the formation of other DBPs (THM, ClO_2^- and ClO_3^-) in lake water (SW I) at (a) pH 6.0 and (b) pH 7.8. High doses correspond to 1.4 mg/L of ClO_2 and/or 2.2 mg/L of Cl_2 and low doses correspond to 0.7 mg/L of ClO_2 and/or 1.1 mg/L of Cl_2.

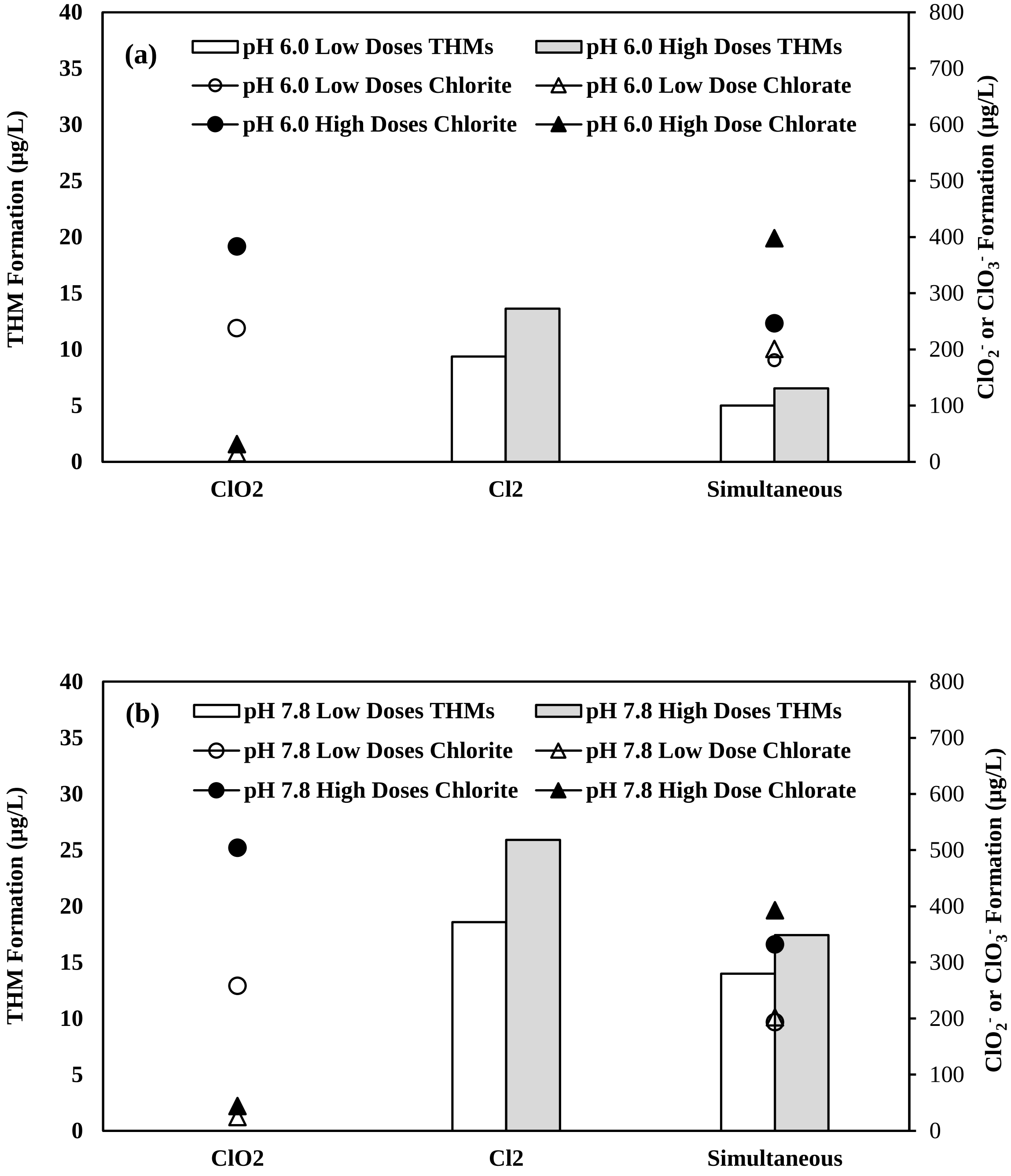


Figure 8.13. The effect of individual and selected oxidation strategies on the formation of other DBPs (THM, ClO_2^- and ClO_3^-) in impacted water 1 (IW 1) at (a) pH 6.0 and (b) pH 7.8. High doses correspond to 1.4 mg/L of ClO_2 and/or 2.2 mg/L of Cl_2 and low doses correspond to 0.7 mg/L of ClO_2 and/or 1.1 mg/L of Cl_2.

Conclusions

In non-impacted natural waters, NDMA FP removal was low (<25%) after oxidation with Cl_2 and/or ClO_2 independent of oxidation pH. However, higher NDMA FP removals were observed in WW-impacted waters indicating that reactive precursors toward those oxidants are present in treated WW effluent waters. In WW-impacted waters, high oxidation pH (i.e., 7.8) significantly increased the removal of NDMA FP up to 73% and 58% compared to low pH (6.0) for ClO_2 and Cl_2, respectively. However, integrated oxidation (simultaneous or sequential) significantly improved the removal of NDMA FP at pH 6.0. Accordingly, the formation of NDMA under UFC also decreased (up to 91%) significantly when the ClO_2 and Cl_2 applied simultaneously independent of oxidation pH. Higher oxidant doses (ClO_2=1.4 mg/L and Cl_2=2.2 mg/L) were warranted to achieve maximum benefits.

On the other side, integrated oxidation with Cl_2 and ClO_2 improved (~30-50%) the removal of polymer-derived NDMA precursors compared to individual application of those oxidants. However, sufficient oxidant doses (ClO_2=1.4 mg/L and Cl_2=2.2 mg/L) were required to gain maximum benefits. Simultaneous use of Cl_2 and ClO_2 can be beneficial to decrease regulated THMs and ClO_2^- formations compared to the use of either Cl_2 alone or ClO_2 alone. However, the use of simultaneous oxidation significantly increased the formation of ClO_3^- at pH 6.0 and 7.8. Therefore, the formation of ClO_3^- can be the main concern for integrated oxidation with Cl_2 and ClO_2.

CHAPTER NINE

CONCLUSIONS AND RECOMMENDATIONS

Conclusions

Objective 1: To investigate the NDMA FP levels in various source waters (i.e., rivers and lakes/reservoirs) and their temporal (seasonal and episodic events) variations.

The physical characteristics of watersheds exerted important influence on the seasonal and temporal patterns of NDMA FP in the source waters monitored in this study. In the dam-controlled river system, the NDMA FP levels at the downstream sampling locations were mainly controlled by the NDMA levels in the reservoir independent of water releases or intermittent high NDMA FP levels observed the upstream of dam. The large reservoirs on the rivers acted like equalization basins for NDMA precursors. On the other hand, in a river without an upstream reservoir, the NDMA levels were influenced by the ratio of an upstream wastewater treatment plant (WWTP) effluent discharge to the river discharge rate. The impact of WWTP effluent decreased during the high river flow periods due to rain events. In contrast, NDMA FP in the reservoirs remained relatively consistent during the monitoring period, and individual rain events near the sampling points did not affect NDMA FP levels, except in three limited impacted reservoirs where NDMA FP levels decreased as a result of long term rain events. In most sources, higher variability of NDMA FP was observed in spring months, but seasonal mean values were relatively consistent regardless of season except two sources where the mean values of NDMA FP were higher in spring and summer, respectively. Overall, understanding watershed characteristics and their influence on NDMA FP is important to determine the seasonal and weather related patterns of NDMA precursors in a source water and to develop NDMA control strategies by a water utility. Multiple liner regression analysis between DOC and log [sucralose] with NDMA FP yielded a better correlation than linear correlations between different water quality parameters and NDMA FP. Despite the empirical nature, if proven to be successful, this type of correlation can be useful to estimate NDMA precursor levels in some source waters. The patterns of NDMA precursors in natural waters were different than those of regulated THMs, which provide further evidence that NDMA and THM precursors are different.

Objective 2: To investigate the removal of NDMA FP at full scale WTPs and the occurrence of NDMA in distribution systems.

Almost two years of monitoring of full-scale WTPs with various process configurations (conventional clarification processes [i.e., coagulation, flocculation, and sedimentation], DAF, MF, and RO) and operational conditions (e.g., polymer impact, alum clarification, PAC application, pre-oxidation and primary disinfection with Cl_2 and/or ClO_2, and Ct changes) showed that polymer type and/or dose, PAC application, and oxidation practices influenced the NDMA FP removals during drinking water treatment processes. The average NDMA FP removal efficiency of alum clarification was less than 20%, and different seasons and various weather conditions did not affect the removal of NDMA FP. Under optimized conditions for compliance with USEPA's Stage 2 D/DBP rule, the removal of background NOM by alum may increase the effectiveness of subsequent oxidation with ClO_2 or Cl_2 for NDMA precursor inactivation. The use of DAF as compared to clarification did not make a difference. PAC addition at doses higher than 4 mg/L significantly increased the NDMA FP removal with increasing dose, and showed a good correlation (R^2 >0.71) between PAC dose and NDMA FP removal. The use of Cl_2 or ClO_2 as post-oxidants (without pre-oxidation) resulted in 35% and 27% removals. Pre-oxidation with simultaneous use of Cl_2 and ClO_2 resulted in considerable decreases (51-61 %) in NDMA FP. Supplemental addition of a small dose of Cl_2 (0.4-0.8 mg/L) during ClO_2 (0.5-1.0 mg/L) post-oxidation increased the NDMA FP removal to an average of 46% at one WTP. The total average NDMA FP removal between raw water and the POE at the WTPs examined in this study was about 49%. The average NDMA FP removals at WTPs, in general, were independent of different seasons and weather events such as wet/dry periods and high/low river flow conditions. NDMA occurrences in most of the distribution systems were below 10 ng/L, except for one WTP that had up to 27 mg/L of NDMA in the distribution system. NDMA occurrence levels at this plant, however, decreased to about 8 ng/L as a result of the simultaneous use of ClO_2 and Cl_2 as post-oxidants.

<u>Objective 3:</u> To investigate the effect of ClO_2 oxidation on the removal of NDMA FP in WW-impacted waters and the effect of oxidation pH.

The oxidation pH was an important factor in the control of NDMA formation in wastewater-impacted waters. The ClO_2 oxidation prior to chloramination at pH 7.8 was more effective (up to 4 times higher) than at pH 6.0 for the control of NDMA formation in raw, conventionally treated, and wastewater-impacted waters. The maximum NDMA FP removals were achieved within 5-10 min of oxidation time or 10 mg*min/L of Ct.

Increasing ClO_2 dose (from 0.7 mg/L to 1.4 mg/L) increased NDMA FP removals, especially at pH 7.8 in wastewater-impacted waters. ClO_2 consumption increased with increasing oxidation pH and DOC levels. NDMA FPs in wastewater-impacted waters decreased after simulated natural attenuation processes, but the reactivity of NDMA precursors was water specific. ClO_2 was very effective in controlling NDMA formation in the presence of relatively “fresh” wastewater-derived precursors when applied at pH 7.8. In contrast, the ClO_2 efficiency on the THM FP removals was less than 24% independent of oxidation pH.

Objective 4: To investigate the effect of integrated oxidation with ClO_2 and Cl_2 on the removal of NDMA FP.

In non-impacted natural waters, NDMA FP removal was low (<25%) after oxidation with Cl_2 and/or ClO_2 independent of oxidation pH. However, higher NDMA FP removals were observed in WW-impacted waters indicating that reactive precursors are present in treated WW effluent waters. In WW-impacted waters, high oxidation pH (i.e., 7.8) significantly increased the removal of NDMA FP up to 73% and 58% compared to low pH (6.0) for ClO_2 and Cl_2, respectively. However, integrated oxidation (simultaneous or sequential) significantly improved the removal of NDMA FP at pH 6.0. Accordingly, the formation of NDMA under UFC also decreased (up to 91%) significantly when the ClO_2 and Cl_2 applied simultaneously independent of oxidation pH. Higher oxidant doses (ClO_2=1.4 mg/L and Cl_2=2.2 mg/L) were warranted for the maximum benefits. On the other side, integrated oxidation with Cl_2 and ClO_2 improved (~30-50%) the removal of polymer-derived NDMA precursors compared to individual application of those oxidants.

However, sufficient oxidant doses (ClO_2=1.4 mg/L and Cl_2=2.2 mg/L) were required to gain maximum benefits. Simultaneous use of Cl_2 and ClO_2 can be beneficial to decrease regulated THMs and ClO_2^- formations compared to the use of either Cl_2 alone or ClO_2 alone. However, the use of simultaneous oxidation significantly increased the formation of ClO_3^- at pH 6.0 and 7.8. Therefore, the formation of ClO_3^- can be the main concern for integrated oxidation with Cl_2 and ClO_2.

Recommendations for Practical Applications

- Characterize and understand NDMA FP patterns in the watersheds for identifying the sources of NDMA precursors and developing source control and/or use strategies. The presence of upstream reservoirs, wastewater treatment plant discharges, mixing conditions and other such factors will influence the NDMA FP levels at the intake(s) of a utility.
- Do not rely on the patterns of THM FP and its surrogate parameters like DOC or UV to predict NDMA precursor patterns. DON is also not a good predictor of NDMA precursors.
- Consider using multiple liner regression analysis such as developed in this study between DOC and log [sucralose] with NDMA FP, if correlations are to be developed between NDMA FP and water quality parameters,
- Consider oxidation strategies and PAC adsorption for additional NDMA FP removal in addition to clarification process.

- Consider using ClO_2 and/or Cl_2 with the following strategies for wastewater impacted surface waters: i) simultaneous or sequentially (ClO_2 first) use of ClO_2 and Cl_2 during conventional clarification (at pH ~6.0), ii) post-oxidation with ClO_2 only (preferentially ≥1 mg/L) at pH ~ 8.0, and iii) simultaneous use of ClO_2 and Cl_2 at pH 8.0.
- Due to the possible future regulations of chlorate in drinking water, its formation during the integrated oxidation strategies using ClO_2 needs to be assessed before the implementation.
- Consider ClO_2 and Cl_2 to decrease NDMA FP in polymer-impacted waters (e.g., polyamine, polyDADMAC and polyacrylamide).

Recommendations for Future Research

- Other important sources of NDMA precursors and the effect of natural attenuation processes on such precursors need to be investigated considering watershed dynamics.
- Possible reasons of higher variability observed in spring and summer months needs to be understood especially in anthropogenically and biologically impacted sources.
- Responsible portion(s) of commonly used polymers that are forming NDMA and their fate during the clarification and filtration processes needs to be understood.
- Types of amine precursors that can/cannot be deactivated by ClO_2 or Cl_2 oxidations at higher oxidation pH (>7.8) need to be investigated in depth considering the compound structures especially in WW-impacted waters.
- Intermediates formed during the reaction of ClO_2 and $HOCl/OCl^-$ and its effect on the deactivation of NDMA precursors need to be investigated.

APPENDICES

Appendix A

Source Waters and Water Treatment Plants

In this section, i) selected watershed characteristics for each source waters used by particular WTPs are evaluated and summarized in **Table A.1**, and ii) detailed water treatment configurations of WTPs are also presented.

Water Treatment Plants 1 and 2

Source Water Description for SW A: The intake of WTP 1 and WTP 2 is on a river (SW A) which is approximately 300 miles long. Two major cities, one upstream about 90 miles from the intake and the other downstream, are located along the river. The 1988-90 land cover data showed 56.9% of the basin in forest cover, 8.9% in wetlands, 2.1% in urban land cover, and 8.8% in agriculture. Agriculture is varied with mixture of animal operations and commodity production. Total farmland in the basin, approximately 797,183 acres, has declined rather steadily since 1982. Almost 75% of the farmland is in pasture. The remaining 25% is dedicated to growing cotton, peanuts, tobacco, grain such as wheat, sorghum, soybean, and millet. Livestock and poultry production is relatively intense in the river basin. Therefore, pesticides, fertilizers, and animal waste may constitute the potential sources of NDMA precursors in the river watershed.

The basin is around 9,850 square miles and the flow of the river is controlled by an upstream dam, where the level is controlled by releases from two upper reservoirs. The minimum flow in the river is 2,000 and 2,300 million gallon per day (MGD) during the winter and summer months, respectively. Water released from the lakes is generally low in organic carbon, but inflow from swamps above the intake, due to high release rates, may result in high organic levels (TOC 8-15 ppm) in water. The river receives industrial discharges from paper/chemical companies with about 60 MGD permitted flow and wastewater discharges with about 90 MGD flow. They are located at least 85 miles away from the intake of WTP 1 and WTP 2.

The raw water from the river is pumped into a 60 acre reservoir (180 MG capacity) before entering WTP 1 (**Figure A.1**). Water is drained from that reservoir into canal at a rate up to 4 MGD, depending on the reservoir level. This helps keeping the reservoir water "fresh" and reduces algal growth. WTP 2 receives water from a pond located at the end of a long canal.

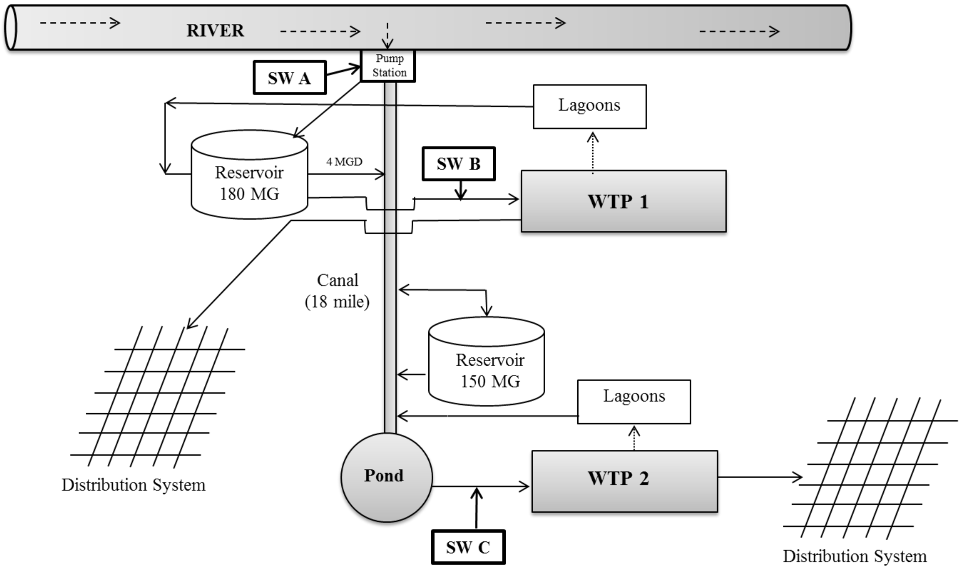


Figure A.1. The intake system of WTP 1 and WTP 2.

Table A.1. Summary of selected characteristics for each source water.

		Watershed land usage				Possible nitrosamine precursor source	
Source	Type	Forest %	Wetland %	Urban %	Agriculture %	Non-point source	Point source
A	River	~57	~8	~2	~8	○ Livestock, Poultry Production	○ Paper/chemical industries discharge ~ 60 MGD (~ 85 miles away from intakes). ○ Domestic discharge ~90 MGD (~ 85 miles away from intake).
D	Reservoir	~70	~7	~11	~5	○ N/A	○ Minor industrial <1 MGD. ○ Minor domestic discharges <1 MGD.
E	River	~46	~21 (swamp) ~13 (marsh)	~0.5	~6	○ Spray irrigation system. ○ Seven mining activities.	○ Minor industrial discharge. ○ Domestic discharge ~9 MGD (~ 40 miles away from intake).
F	Lake	~54	~1 (forested)	~3.1	~11	○ Septic tanks, forested land practices, agricultural activities, urban runoff, spray irrigations, spray field, tile filed, low pressure irrigation.	○ Two minor domestic discharge <1 MGD.
G	River	~59	~3 (forested)	~21	~13	○ Agricultural activities, urban runoff, land disposal and mining activities.	○ Industrial discharge from nuclear station ○ Nine minor industrial discharges. ○ Two minor domestic discharges.
H I J K	Reservoir Lake River Reservoir	~90	None	None	~8	○ Run off from pastures, animal operations, recreational waste.	○ None
L	Lake	~78	~0.1 (swamp)	~4	~7	○ Some recreational destinations (e.g., fishing, boating, swimming, sailing)	○ None
M	Lake	~89	~0.1 (forested)	~3	~5	○ None	○ None
N	Lake	~83	~0.6 (swamp)	~5	~9	○ None	○ None

Water Treatment Plant Process Trains and Typical Operational Conditions for WTP 1: The capacity of WTP 1 is 16 MGD. The treatment process train consists of pre-treatment steps (PAC and chlorine), coagulation-flocculation, sedimentation, filtration, post-disinfection, and storage (**Figure A.2**). Under a typical operational condition, water residence time is approximately 1 hour between the intake and filters, and 2-3 hours in the clearwell. *Intake.* The raw water from SW A is pumped into the reservoir at a rate of 3 to 9 MGD. Water is drained form the reservoir, which has 180 MG capacity, into the canal at a rate up to 4 MGD and transmitted to the plant for the treatment. The sampling location SW B was selected to monitor the water quality at the plant influent. *Pre-treatment.* PAC may be added before pre-oxidation. Cl_2 may be used at the dose of 0.8 ppm, as needed basis, to prevent any algae growth and other microbial activities in the treatment basins, pipes and conduits.

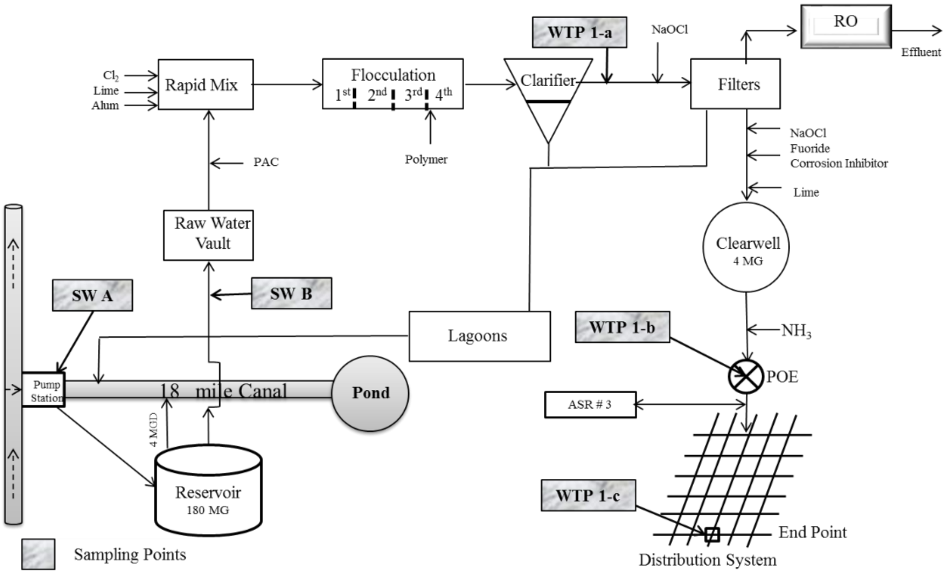


Figure A.2. Schematic diagram of WTP 1.

Coagulation-Flocculation. Water goes through rapid mix and 4-stage flocculation and then is split into two identical and parallel process trains. During normal operations, the plant uses both trains. Under a typical operation condition, alum (28 ppm), lime (3-4 ppm), and Optimer Nalco Pulv 8110 (~0.02 ppm) is added in the pre-chemical feed station. The pH is maintained around 6.2 in the rapid mixers. *Sedimentation.* The plant has plate settlers. The basin sludge goes to the alum ponds then the supernatant is discharged to the 18 mile canal. After the clarifiers, about 1.0 ppm NaOCl is added in water to maintain residual targets of 0.10-0.15 ppm in the filter effluents. When manganese levels exceed 0.06 ppm, the pre-filter chlorine is increased to maintain 0.20-0.25 ppm in the filter effluents. *Filtration*. Suspended particles and flocs in water after the settlers are removed by the dual media filters consisting of anthracite and sand. The filter backwash water, after settling in lagoons, is discharged to the canal. The plant has also a small RO system that is used as needed basis to supply water to a nearby power plant. RO effluent is not mixed with the treated water and not pumped to the distribution system. *Post-oxidation and storage*. Chlorine (2.5-3.0 ppm of NaOCl), fluoride, and corrosion inhibitor (Ortho/Poly phosphate blend 50/50) are added. Then, lime is added just before the transfer station to the clearwell. In the clearwell with 4 MG capacity, the detention time is approximately 7-8 hours under typical flow conditions. NH_3 is added after the clearwell with a target Cl_2:NH_3 weight ratio of 4:1 to maintain combined chlorine residual of 2.5-3.0 ppm at the point of entry (POE).

Water Treatment Plant Process Trains and Typical Operational Conditions for WTP 2: The capacity of WTP 2 is 24 MGD. The water treatment process train consists of raw water intake, PAC addition, coagulation-flocculation, sedimentation, filtration, post-oxidation, and storage (**Figure A.3**). Under a typical operation condition, water detention times are about 6 hours between the intake and filters, and 1.5 to 4.5 hours in the clearwells

Intake. The raw water is pumped from the pond at the end of the canal into the plant. The sampling location (SW C) was selected to monitor the water quality at the plant influent.

Coagulation-Flocculation. Before rapid mixing, plant water is split into two identical process trains with the same configuration, the same operation, and similar performance. PAC (up to 7 ppm) may be added for taste and odor control.

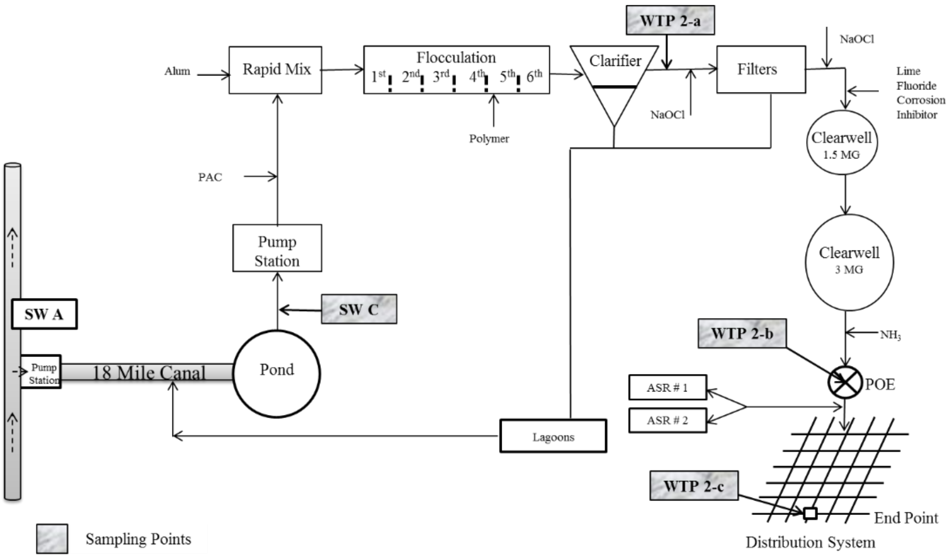


Figure A.3. Schematic diagram of WTP 2.

During normal operations, WTP 2 uses both trains in parallel. About 40 ppm of alum is used along with lime (~10 ppm), and pH is maintained at 5.6 to 6.4 in the rapid mixers. Optimer Nalco Pulv 8110 (~0.02 ppm) is added in the fifth basin of the flocculation unit. *Sedimentation.* The plant has lamella settler type clarifiers. Settled flocs are removed and piped to a WWTP. After sedimentation, 0.9-1.0 ppm of NaOCl is added to maintain a target of ~0.10 ppm in the filter effluents. *Filtration.* The plant has dual media filters that consist of anthracite and sand. The filter backwash water, after settling in lagoons, is discharged back to the pond. *Post-oxidation and storage.* Clarified and filtered water passes through two clearwells with 1.5 MG and 3.0 MG capacity, respectively, and the detention time is approximately 1.5 to 4.5 hours. Then, NH_3 is added at the Cl_2:NH_3 weight ratio of 4:1 to maintain 2.0-2.5 ppm combined chlorine residual at POE. Other additives in the clearwells are fluoride to prevent tooth decay, and Ortho/Poly phosphate 50/50 as a corrosion inhibitor. The treated water is pumped to the distribution system.

Distribution Systems for WTP 1 and WTP 2: The distribution system is divided in two areas; North of Broad (NOB) and South of Broad (SOB). WTP 2 serves the NOB and supplements WTP 1 to the SOB, although the capability to connect the two sides of the system and the use of either WTP 1 or WTP 2 to supply the entire system in the event of an emergency are optional. Three groundwater wells are used for the peak periods in the SOB area. These wells have excellent water quality that can be used with only chloramine disinfection. The NOB system has 7.9 MG of storage in 14 elevated/ground tanks. The SOB system has 4.5 MG of storage in 7 elevated/ground tanks. Fifty percent of the NOB system has <1 day of detention time, 35% 2-3days, and 15% >4 days. Sixty five percent of the SOB system has <1 day of detention time, 30% 2-3 days, and 5% >4 days. The distribution system sampling locations for the two WTPs in this study were carefully selected to assure that the water at each location is fed from one single plant. The WTP 1-c site represents the longest detention time from WTP 1 with a typical detention time of 1 day, while WTP 2-c is fed from WTP 2 with a typical detention time of 5 days.

Water Treatment Plant 3

Source Water Description for SW D and SW E: WTP 3 has two water sources, SW D and SW E. The plant typically withdraws 95% of its raw water from SW D and 5 % from SW E. The source of SW D reservoir is an upstream river whose watershed occupies 49,168 acres. Land use/land cover in the watershed includes 70.7% forested land, 11.9% urban land, 7.5% forested wetland, 5.1% agricultural land, 3.0% scrub/shrub land, 1.4% water, and 0.3% barren land. There are a total of 87.3 stream miles, 287.1 acres of lake waters, and 80.3 acres of estuarine areas in this watershed. Water quality variation may be attributable to both point and nonpoint sources. The national pollutant discharge elimination system (NPDES) permits exist of three point sources, among them are classified as minor (i.e., <1 MGD) industrial and minor domestic.

Another source water of WTP 3 is a river (SW E) whose watershed occupies 159,521 acres of the coastal plain and coastal zone regions. Land use/land cover in the watershed includes 46.4% forested land, 21.6% forested wetland (swamp), 13.8% non-forested wetland (marsh), 9.0% water, 6.1% agricultural land, 2.6% barren land, and 0.5% urban land. There are a total of 143.3 stream miles, 132.1 acres of lake waters, and 8,683.1 acres of estuarine areas in this watershed. Average annual stream flow on SW E is 1,690

MGD. There are one minor industry NPDES permit, two listed non-point sources, spray irrigation systems, and seven mining activities (sand/clay as type of minerals). Also, there is domestic discharge ~9 MGD (~ 40 miles away from intake).

Water Treatment Plant Process Trains and Typical Operational Conditions* for *WTP Three: WTP 3 has been designed with a capacity to produce 118 MGD and produces an average of 58 MGD (**Figure A.4**). *Intake.* The plant typically withdraws 95% of its demand from SW D and 5 % from SW E. PAC is added at the pump station to control taste and odor as needed basis. *Coagulation-Flocculation.* The flow is split into two parallel and identical trains. The plant uses alum for coagulation at a typical dose of 40-50 ppm. The pH is maintained at 5.9-6.1. Polyacrylamide (Nalco 8170, ~0.03 ppm) is added in the fourth basin of the flocculation unit. *Sedimentation.* Clarifiers are used to separate flocs from water. After the clarifiers, ClO_2 is added at the top of the filters at a dose ranging from 0.1 to 0.3 ppm. *Filtration.* The plant has multimedia (anthracite, sand, gravel) rapid deep bed filters. Since the utility`s research has found ClO_2 to be beneficial on filter run time, ClO_2 is added on top of the filters. After the filters, fluoride and corrosion inhibitor (H_3PO_4) are added. *Post-oxidation with ClO_2 and/or Cl_2.* To obtain Ct credits, the plant used ClO_2 after the filters in two clearwells (#2 and #3) in the first 6 months of the monitoring study. After six months, Cl_2 was applied simultaneously in addition to ClO_2. The oxidant doses applied to clearwells were in the range of 0.2-0.7 ppm for ClO_2, and 0.4-1.0 ppm for Cl_2. After these two clearwells, caustic, chlorine and ammonia are added at clearwell #3 effluent, while lime, chlorine, and NH_3 are added at clearwell #2 effluent. Clearwell #4 serves as storage. The effluent pH of water leaving the plant is in the range of 8.0 to 8.5.

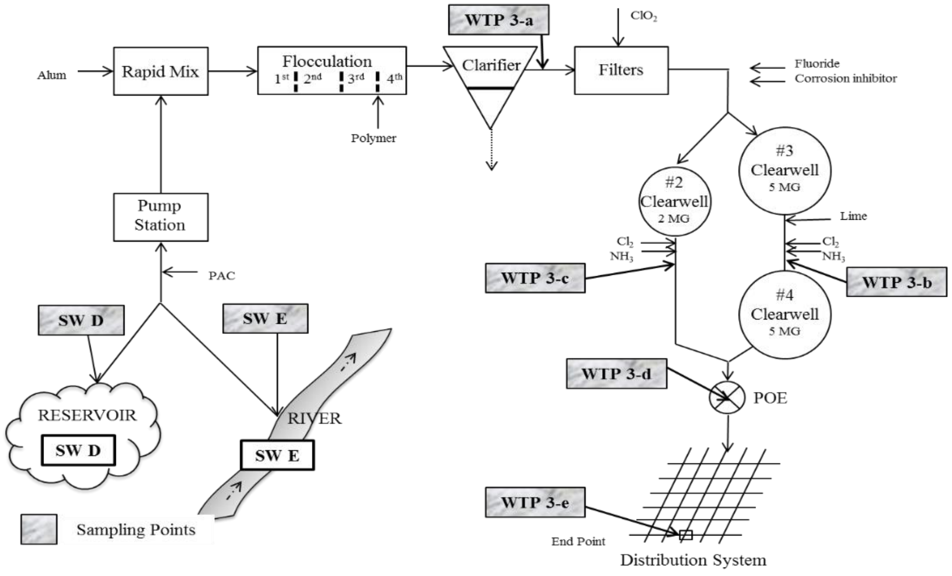


Figure A.4. Schematic diagram of WTP 3.

Distribution System for WTP 3: The sampling location selected for this study is one of the longest residence time locations in the distribution system with an average detention time of ~15 days at typical operations. However, the water age can be higher depending on demand fluctuations.

Water Treatment Plants 4 and 5

Source Water Description for WTP 4 and SW F: The two upper river watersheds merge to form the headwaters of a lake (SW F). Land use/land cover in the watershed includes 54.3% forested land, 29.1 % water, 11.7% agricultural land, 3.1 % urban land, 1.1 % forested wetland (swamp), 0.6% barren land, and 0.1 % non-forested wetland (marsh). The lake's watershed is 1,193 square miles.

There are some point and nonpoint discharges around the lake. These discharges include pesticides/herbicides, volatile organic carbon (VOCs), and some other compounds. There is also considerable number of septic tanks around the lake. SW F receives two minor (<1 MGD) domestic WWTP discharges. The non-point sources include land application, land disposal, and mining activities. The land application activities include spray irrigation, spray field, tile field and low pressure irrigation, All these sources have potential domestic pollutants. In addition, there are one closed domestic landfill and two shale mining facilities within the lake watershed. Other possible non-point sources include forested land, urban land, agricultural land, and forested wetland. Forested land practices associated with road access, harvest, and regeneration of timber may cause addition of sediment, nutrients, organics, elevated temperature, and pesticides. Pesticides, fertilizers, animal waste, and sediment are potential sources due to agricultural activities. The major pollutants are found in runoff from urban areas include sediment, nutrients, oxygen-demanding substances, heavy metals, petroleum hydrocarbons, pathogenic bacteria, and viruses.

Water Treatment Plant Process Train and Typical Operational Conditions for WTP 4: The capacity of WTP 4 is 75 MGD and the daily average is typically 35 MGD. The water treatment process train consists of raw water intake, pre-treatment, coagulation-flocculation, sedimentation, filtration, post-oxidation, and storage (**Figure A.5**). Water detention time between the intake and clearwells influent is about 11 hours at the typical flow rate of 35 MGD. *Intake.* The raw water is pumped into the treatment plant from a midpoint elevation in the raw water pump station to minimize swings in water quality throughout the year. The intake is equipped with screens to keep floating debris, plants, and fish away from the plant. *Pre-treatment.* ClO_2 is used as primary disinfectant at 1.0-1.5 ppm at the raw water pump station. About 2-3 ppm (or higher depending on MIB and geosmin levels) of PAC is also added at the same location as needed basis. Before the rapid mixing, 1.0 ppm of Cl_2 is added to keep the basins clean and as a backup oxidant in case the ClO_2 feed system experiences any problem. The time interval between ClO_2/PAC and Cl_2 addition is approximately 10 minutes at 35 MGD. Operating residual is maintained at 0.5-1.5 ppm in the rapid mixing basins 1 and 2. *Coagulation-Flocculation*. Before the rapid mixing, plant water is split into two parallel process trains with the same configuration, same operation, and similar performance. During normal operations, the plant uses both trains. Average doses of 25-30 ppm alum is added into water at the control building. The target pH is maintained at 6.2. In the rapid mixing unit, typically 0.25 ppm of cationic polyacrylamide polymer (Sedifloc 400C, maximum allowed dose of 3 ppm) is added. The water detention time is typically around 10 minutes between the intake and the rapid mixing. *Sedimentation.* Settled flocs at the bottom are removed and piped to a WWTP. After sedimentation, 0.5-1.0 ppm of Cl_2 is added to maintain a target 0.3 ppm of chlorine residual. *Filtration.* The filters are designed as dual media consisting of anthracite and sand. *Post-oxidation and storage.* Before clearwells, 3.5 ppm of Cl_2 is added. There are 2 clearwells with 5 MG capacity in series. The detention time is approximately 96 and 205 minutes at maximum flow of 75 MGD and average flow of 35 MGD, respectively. Immediately after the clearwells, NH_3 is added to maintain 3.2-3.5 ppm of combined chloramines at POE. The typical Cl_2:NH_3 weight ratio is 3.5-4.0:1. Other additives in the clearwells are lime for pH adjustment, fluoride to prevent tooth decay, and orthophosphate for corrosion control. The pH ranges from 7.8 to 8.2 at POE.

Distribution Systems for WTP 4: Maximum water age in the distribution system is approximately 4 days. One of the longest detention points on the distribution system was selected for sampling in this study.

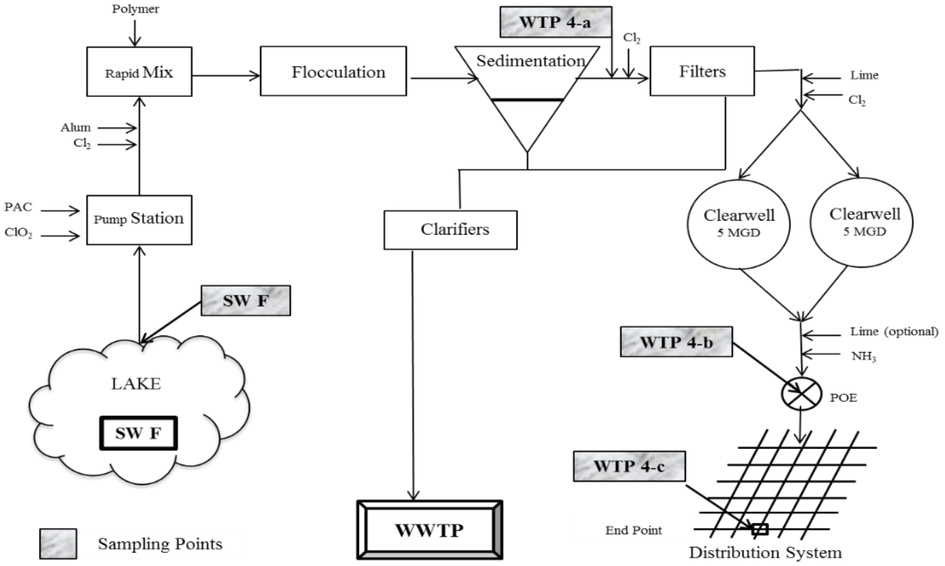


Figure A.5. Schematic diagram of WTP 4.

Source Water Description for WTP 5 and SW G: The source water of WTP 5 is a river (SW G) which is approximately 274 miles long. The river watershed occupies 148,599 acres. Land use/land cover in the watershed includes 59.4% forested land, 21.4% urban land, 13.0% agricultural land, 3.0% forested wetland, 2.0% water, 0.8% barren land, and 0.4% scrub/shrub land. In 2007, the flow rate (annual minimum 7-day average stream flow with a 10-year recurrence interval) of the river was 394 MGD.

In this watershed, point sources are primarily WWTPs and industrial dischargers. The river receives one major industrial discharge from a nuclear station and nine minor industrial discharges from hydro station, quarry, nuclear training center, brick, vulcan materials, and creek tributary. Two major and one minor discharges are coming from domestic wastewater treatment utilities. The closest upstream wastewater discharges are a county WWTP (10 miles upstream) and a city WWTP (13 miles upstream) with about 6 MGD and 1.5 MGD permitted flow, respectively. The non-point sources include land disposal and mining activities. In the river watershed, there are three closed domestic and four closed construction and demolition (C&D) dump and landfill sites, one closed sanitary landfill site, three inactive C&D landfill sites, one inactive composting facility, four active C&D landfill sites, one active incinerator facility, one active land application, and two proposed construction and landfill activities. Other possible non-point sources include forested land, urban land, agricultural land, and forested wetland. Forested land practices associated with road access, harvest, and regeneration of timber may cause addition of sediment, nutrients, organics, elevated temperature, and pesticides. Pesticides, fertilizers, animal waste, and sediment are potential sources of agricultural activities. The major pollutants are found in runoff from urban areas include sediment, nutrients, oxygen-demanding substances, heavy metals, petroleum hydrocarbons, pathogenic bacteria, and viruses.

Water Treatment Plant Process Trains and Typical Operational Conditions for WTP 5: A canal of 3-4 miles diverts water from the river to the treatment plant intake. The capacity of WTP 5 is 71 MGD and the daily average operational flow rate is typically 35 MGD. The water treatment process consists of raw water intake, pre-treatment, coagulation-flocculation, sedimentation, filtration, post-oxidation and storage (**Figure**

A.6). Water detention time between the raw water vault and clearwells is about 9 hours at the typical flowrate of 35 MGD. *Intake.* The intake is located on the canal, and the water is collected in a reservoir which has 70 MG capacity with approximately 1 day detention time. However, due to piping of the water in and out of the reservoir, the utility anticipates that the real residence time is much shorter than one day. The main purpose of the reservoir is storage for emergencies. *Pre-treatment.* ClO_2 is used as primary disinfectant at 1.0-2.0 ppm in the raw water vault. At the same location, approximately 1 ppm of Cl_2 is also added. The goal is to have a target Cl_2 residual of 0.3-0.5 ppm at the sedimentation basin effluent flume. *Coagulation-Flocculation.* Alum (average alum dose of 22 ppm) and PAC (2 ppm or higher depending on MIB/geosmin levels) are added at the rapid mixing basin. Cationic polyacrylamide polymer (Sedifloc 400C, average dose of 0.25 ppm) is added at the beginning of the third stage flocculator). Target pH for coagulation-flocculation is 6.2-6.5. *Sedimentation.* Settled flocs at the bottom are removed and piped to a WWTP. After sedimentation, 0.5-1.0 ppm of Cl_2 is added on top of the filters. *Filtration:* The filters are designed as dual media consisting of anthracite and sand. *Post-oxidation and storage*. After the filters, Cl_2 and NH_3 are added to maintain 3.2-3.5 ppm combined chloramines at POE. The target Cl_2:NH_3 weight ratio is 4.0:1. Then, water enters in two clearwells having 3 MG capacity in parallel. The detention time at the typical flow of 35 MGD is 2 hours. Other additives added before entering clearwells are lime, fluoride, and orthophosphate. The pH is 7.8-8.2 at POE.

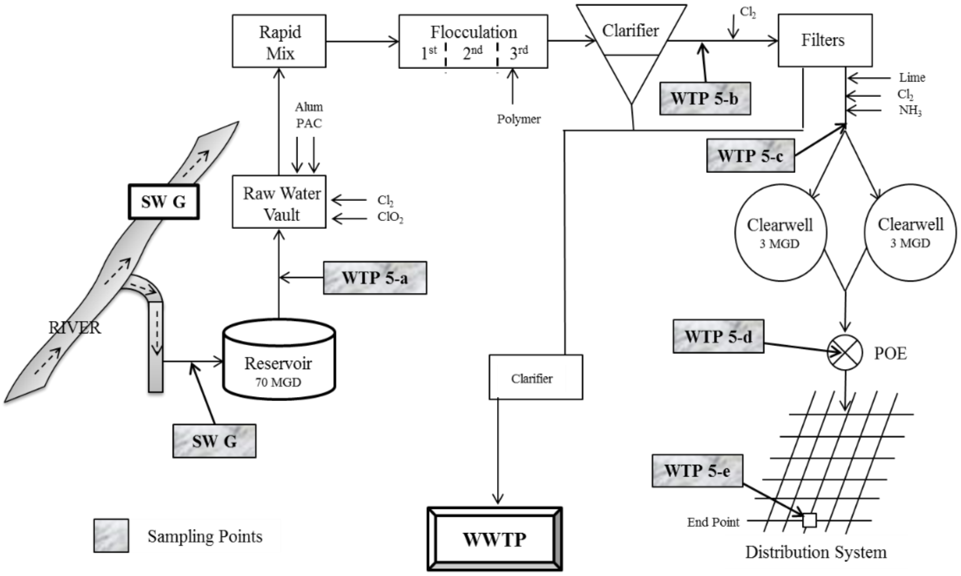


Figure A.6. Schematic diagram of WTP 5.

Distribution Systems for WTP 5: Maximum water age in the distribution system is approximately 5 days. One of the longest detention points on the distribution system was selected for sampling in this study.

Water Treatment Plants 6 and 7

Source Water Description: SWs H, I, J and K: The primary water source of WTP 6 is a river (SW J) which is fed by a 412-acre lake (SW I) approximately 8 river miles upstream the treatment plant (**Figure A.7**). A small creek which flows from a pond (SW H) is a tributary that contributes in the range of 5 to 30% flow in the river. There is another source water that comes from SW K (137-acre reservoir). WTP 6 receives water from both SW J and SW K, while the source water for WTP 7 is SW K alone. As there are no point sources in the river watershed upstream of the WTPs, potential NDMA precursor loadings can be attributed to nonpoint sources. The land use in the watershed is 90.9% forest, 7.9%

agriculture/grass, and 1.3% other. Runoff from pastures, animal operations, and recreational waste can be potential sources of NDMA precursors in these source waters. Historically, there has been high level of biological activities (i.e., algae growth during summer) in the pond SW H.

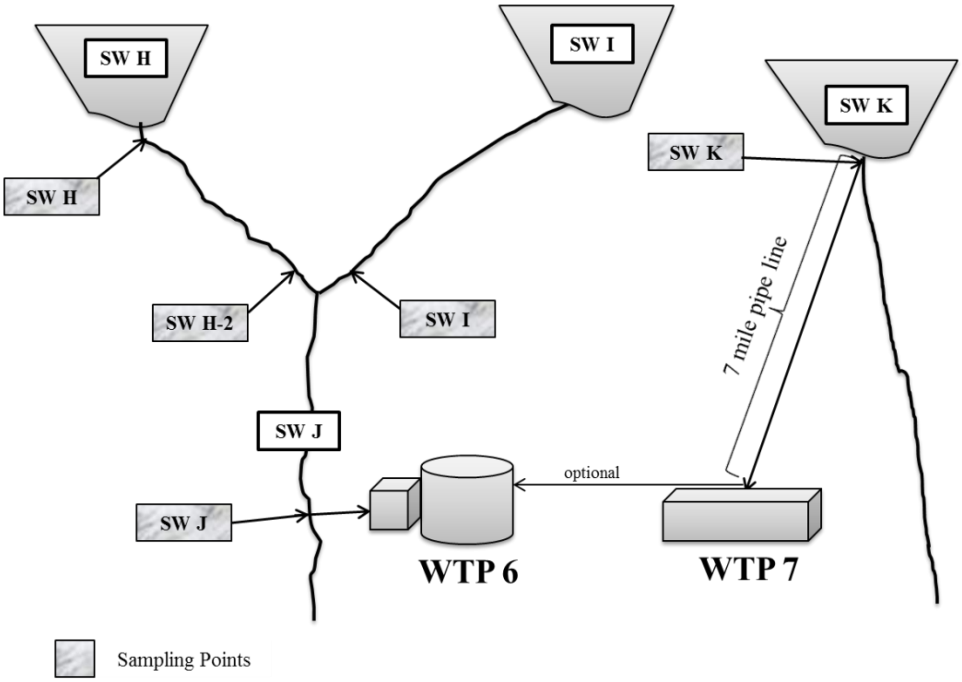


Figure A.7. Water sources of WTP 6 and WTP 7.

The utility is operating a conventional treatment plant (WTP 6) and a newly built microfiltration plant (WTP 7) which began operation in September 2012. The process flow diagram and typical operational conditions of the plants are shown in **Figures A.8 and A.9.**

Water Treatment Plant Process Trains and Typical Operational Conditions for WTP 6: The capacity of WTP 6 is 12 MGD. The water treatment process consists of raw water intake, coagulation, flocculation, sedimentation and oxidation on top of filters for manganese removal, filtration, post- oxidation, and storage (**Figure A.8**). Water detention time is about 1 hour between the intake and filters. *Intake.* Raw water is pumped into the plant primarily from SW J and SW K for the treatment. *Coagulation-Flocculation.* Alum (~20-30 ppm) and hydrated lime are added in the rapid mixers. The pH of water is maintained at around 6.3-6.7 in the rapid mixers. *Sedimentation.* The flocs are separated in the sedimentation basins. *Filtration:* After sedimentation, 0.5-1 ppm of NaOCl is added before dual media filtration and another 1-2 ppm of NaOCl after filtration. Corrosion inhibitor, hydrated lime, and fluosilicic acid are added to the stream before the clearwell. *Post-oxidation with chlorine*. The plant uses NaOCl as the post disinfectant. The treated water passes through 0.75 MG clearwell and 5 MG ground storage tanks. The finished water is pumped to distribution system with 1.0-1.5 ppm chlorine residual. The pH at POE is about 7.2 to 7.4.

Water Treatment Plant Process Trains and Typical Operational Conditions for WTP 7: The capacity of the microfiltration membrane plant is 4 MGD. The water treatment process consists of coagulation, flocculation, sedimentation, microfiltration, post-oxidation, and storage (**Figure A.9**). *Intake.* Raw water is pumped to the plant from SW K through a 7 mile transmission line. *Coagulation and Flocculation.* Alum (20-30 ppm) is added before the flocculation basin, where pH is maintained around 6.5. *Sedimentation:* Flocs are removed using plate settlers. *Microfiltration.* After sedimentation, water passes through microfiltration (Pall) membrane units. For post oxidation, 1-2 ppm of NaOCl is added after the membranes. Corrosion inhibitor and lime are added to water before entering

5 MG ground storage tank. The treated water is pumped to distribution system with 1.0-1.5 ppm of chlorine residual.

Distribution System for WTP 6 and WTP 7: Maximum water age in the distribution system is approximately 7 days. One of the longest detention points on the distribution system was selected for sampling in this study.

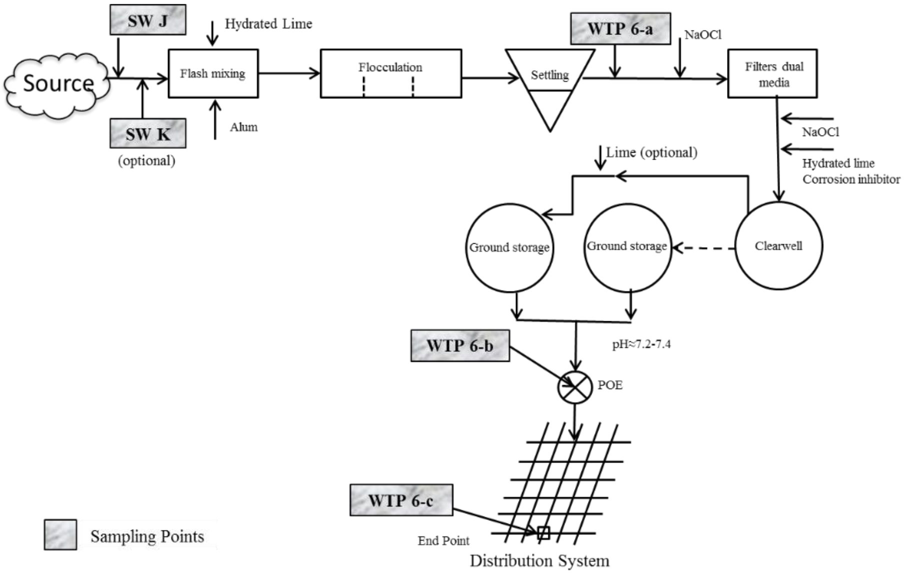


Figure A.8. Schematic diagram of WTP 6.

Water Treatment Plants 8 and 9

Source Water Description for WTP 8 and SW L: WTP 8 draws raw water from a lake (SW L). The lake is a man–made reservoir, which is approximately 26 miles long, 3 miles wide, with an average depth of 54 feet, and a shoreline measured at 300 miles in total, and is approximately 800 feet above sea level. The lake collects or impounds waters from two main rivers and others. Lake water helps to cool three nuclear reactors located several miles away from the intake, and is used to generate hydroelectric power. The lake is also used as a recreational destination for fishing, boating, swimming, sailing, kayaking and other watersports, and the lake has been described as having pure and clean water. Land use/land cover in the extended watershed includes 78.1% forested land, 9.6% water, 7.6% agricultural land, 4.0% urban land, 0.6% barren land, and 0.1% forested wetland (swamp). There is no major point source around the lake.

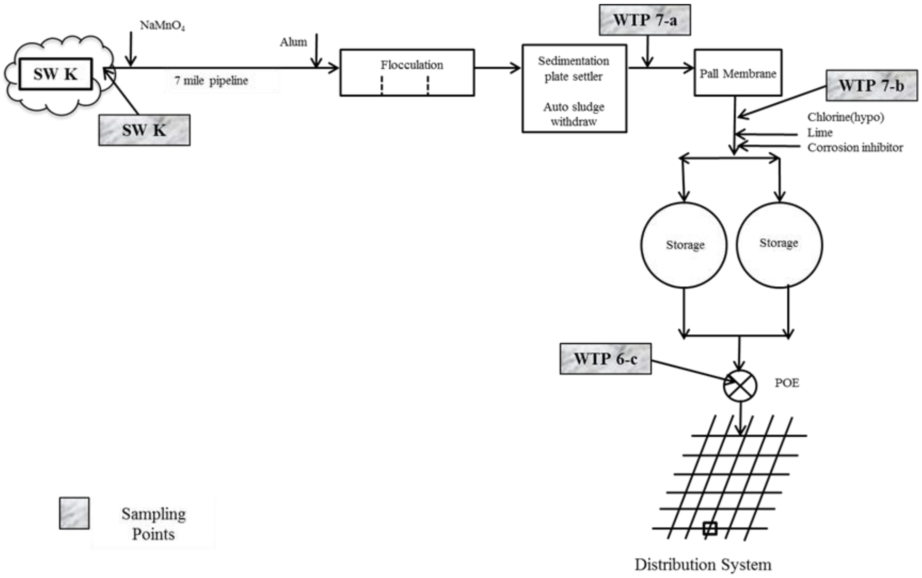


Figure A.9. Schematic diagram of WTP 7.

Water Treatment Plant Process Train and Typical Operational Conditions: WTP 8. The capacity of WPT 8 is 60 MGD and daily average is typically 24 MGD in winter and 32 MGD in summer. The water treatment process consists of coagulation and flocculation, sedimentation, filtration, post-oxidation, and storage (**Figure A.10**). Water detention time between the intake and plant influent is about 7 hours at the typical flow rate of 24 MGD. *Intake.* The intake is located on the lake SW L and intake water is transferred to two parallel and identical trains (east and west). *Coagulation-Flocculation.* Typically, 3 ppm of chlorine is added in the beginning of treatment, followed by 6 ppm of alum, 2 ppm of NaOH (for pH adjustment) and NH_3 addition in rapid mixing units where pH is kept at around 6.2. Therefore, chloramine forms at the entry of the plant between March and September. However, from October to February, chlorine is added at the beginning of the treatment train, while NH_3 is added between conventional treatment and the clearwells to maintain combined chlorine residual levels at 2.5 ppm at the plant effluent. *Sedimentation and Filtration*. Settled flocs at the bottom are removed and piped to large storage lagoons. Clean water from the top of the settling basin is sent to the filters. The filters are dual media high rate filters. *Post-oxidation and Storage.* Cl_2 and NH_3 are added simultaneously in the finished water year round, to maintain a target combined chlorine concentration of 2.5 ppm. The weight ratio of Cl_2:NH_3 is 3.5-4.0:1. After filters, water enters two parallel clearwells with 10 MG capacity. The detention time at the typical flow of 35 MGD is 2 hours. Other additives added before entering clearwells include caustic, fluoride, and zinc polyphosphate. The plant effluent pH is in the range of 7.8-8.2.

Distribution Systems for WTP 8: Maximum water age in the distribution system is approximately 10 days. One of the longest detention points on the distribution system was selected for sampling in this study.

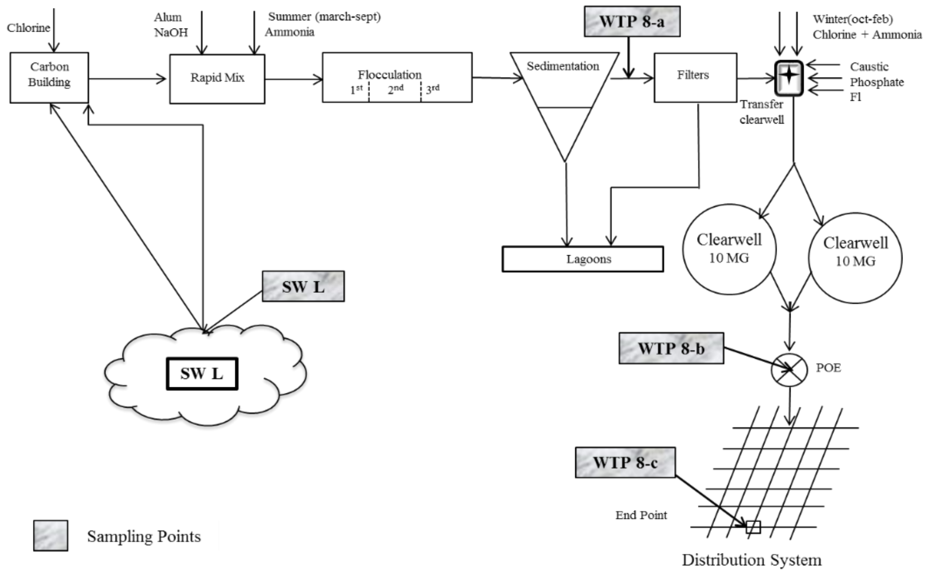


Figure A.10. Schematic diagram of WTP 8.

Source Water Description for WTP 9, SWs M and N: Water from two different reservoirs (SW M and SW N) which are at the head of two different rivers is treated by WTP 9. Land use/land cover in the SW M watershed includes 89.2% forested land, 5.6% agricultural land, 3.0% urban land, 2.1% water, and 0.1% forested wetland (swamp). Land use/land cover in the SW N watershed includes 83.9% forested land, 9.6% agricultural land, 4.8% urban land, 0.6% water, 0.6% forested wetland (swamp), and 0.5% barren land. The utility owns the watersheds of these two reservoirs. As a result, there are no major or minor point/nonpoint sources to impact water quality. These are well protected water sources.

Water Treatment Plant Process Train and Typical Operational Conditions: WTP 9. WTP 9 withdraws raw water from two reservoirs (SW M and SW N) and most of the time blends the waters 50/50. The capacity of WTP 9 is 75 MGD and daily average is typically 24 MGD in winter and 50 MGD in summer. The water treatment process consists of coagulation and flocculation, dissolved air floatation (DAF) system, filtration, post-oxidation and storage (**Figure A.11**). *Coagulation-Flocculation.* Approximately 7.5 ppm of alum and 1 ppm of caustic are added, and pH is maintained at around 6.2 during coagulation-flocculation. Water flows through flocculation basins where vertical mixers blend water with alum. *DAF.* Compressed air is injected at the entrance of the flotation basin. Small air bubbles create a float blanket forcing the floc particles to the surface. Once on top, reciprocating scrapers periodically scrape the residuals off to undergo further treatment and subsequent disposal. *Filtration.* Before filtration, approximately 2.2 ppm of chlorine is added to water. Deep bed mono-media (anthracite) filters are used. *Post-oxidation.* After filtration, 1 ppm of chlorine and 7 ppm of NaOH added to adjust pH at 7.8-8.2 before entering two parallel clearwells having 2.5 MG capacity each. The detention time at the typical flow of 50 MGD and 25 MGD are 2.4 and 2.8 hours, respectively. After the clearwells, NH_3 is added to water at the Cl_2:NH_3 weight ratio of 4:1. Fluoride and corrosion inhibitors are added before the distribution system. The water at POE to the distribution system has 2.5 ppm of total combined chlorine residual and pH of 7.5-8.0.

Distribution Systems for WTP 9: Maximum water age in the distribution system is approximately 7 days. Two representative sampling locations with the longest detention points on the distribution system were selected for monitoring in this study.

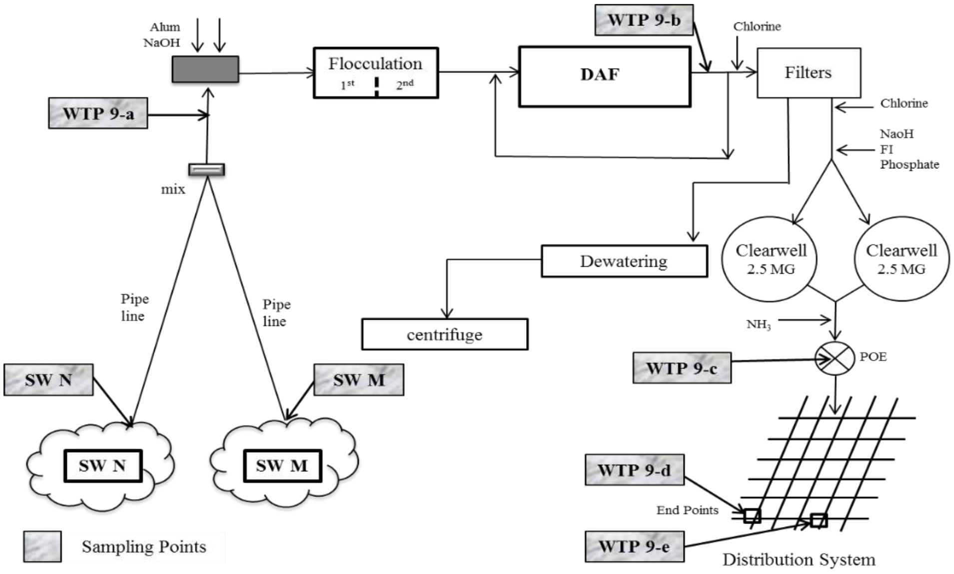


Figure A.11. Schematic diagram of WTP 9.

Sample Calibrations for Nitrosamines that were detected by USEPA Method 521

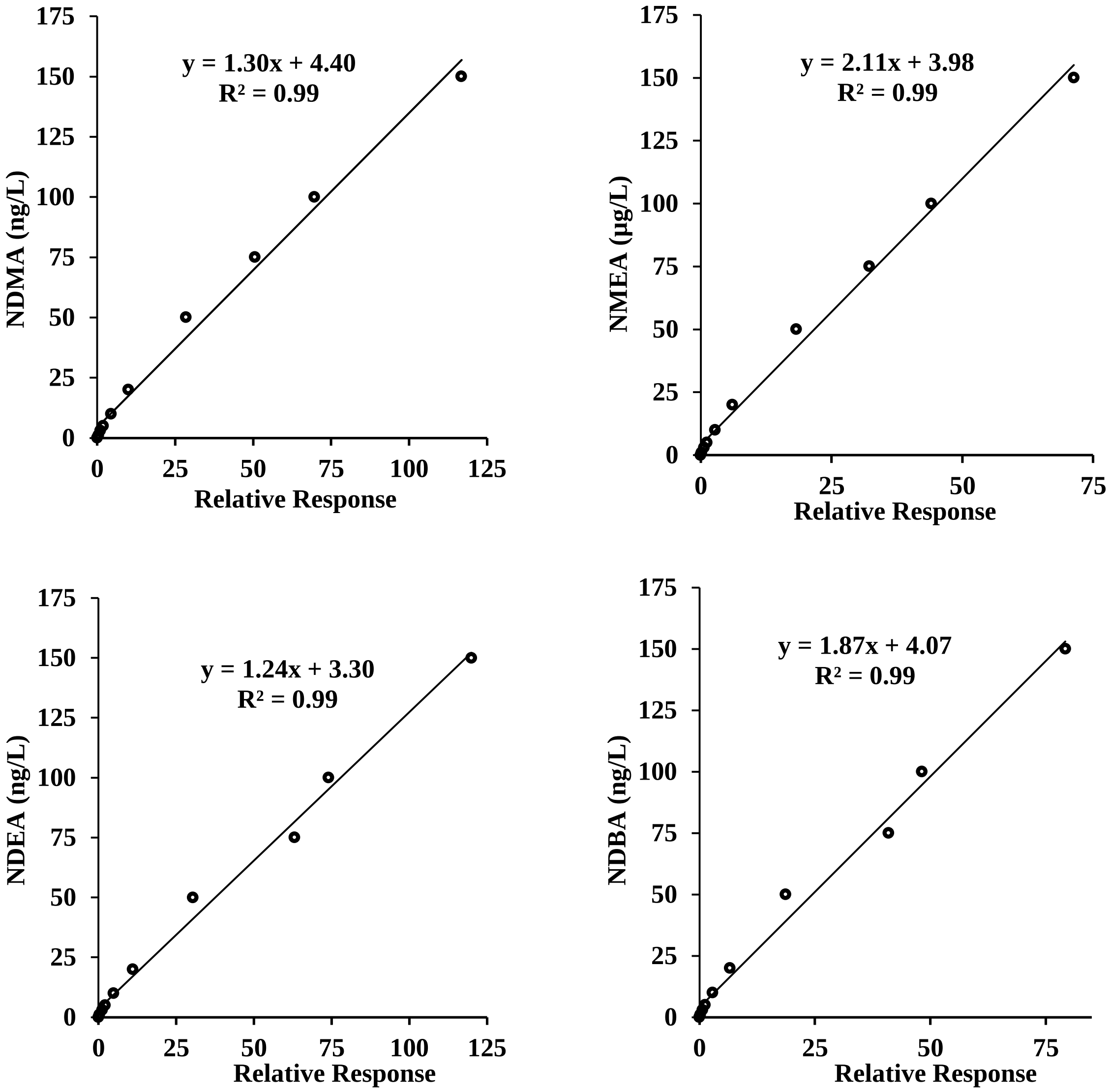


Figure A.12. A representative calibration curve for (a) NDMA, (b) NMEA, (c) NDEA and (d) NDBA.

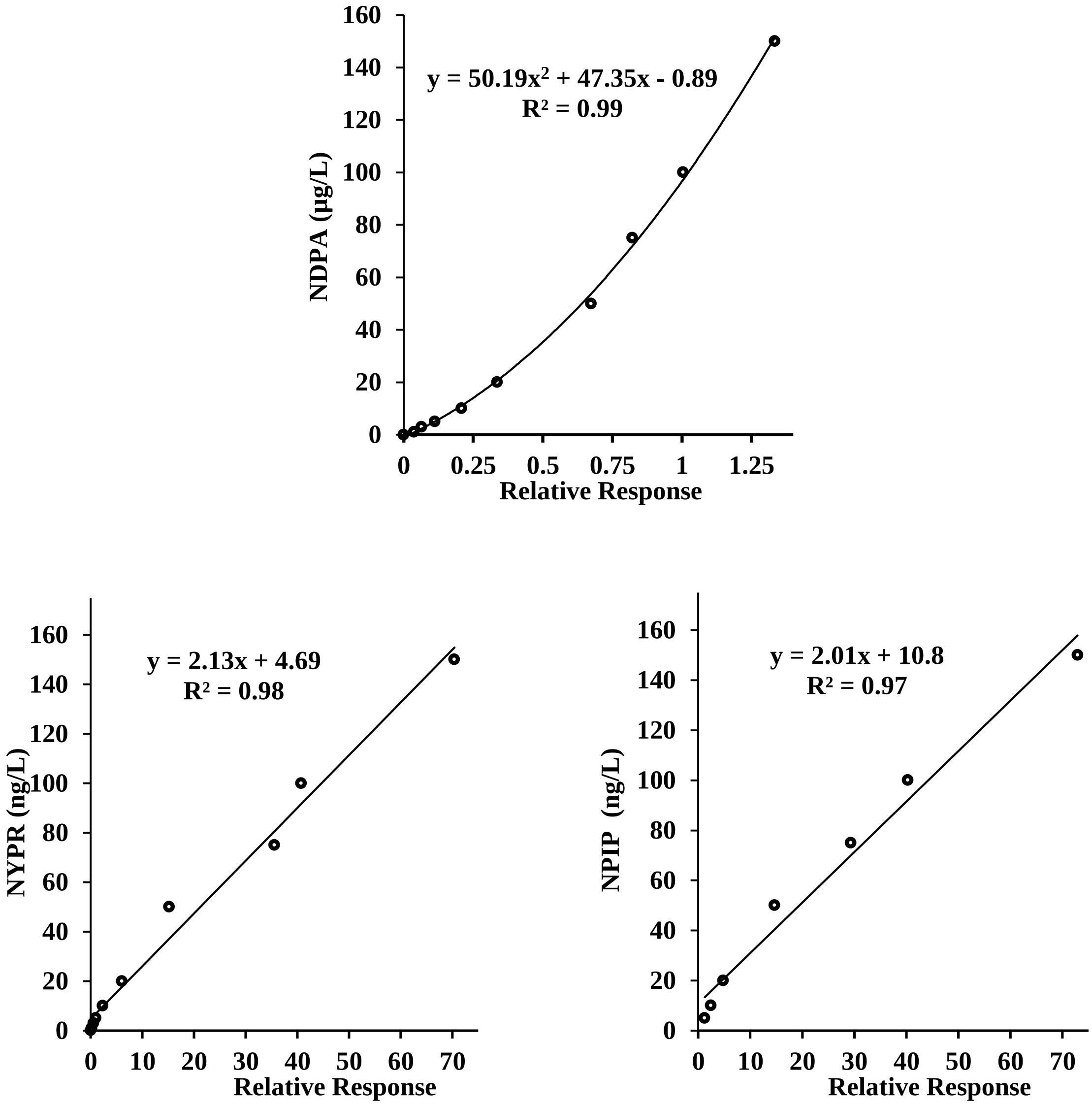


Figure A.13. A representative calibration curve for (a) NDPA, (b) NYPR and (c) NPIP.

Appendix B

Supplemental Information for Chapter Five

Table B.1. Occurrence levels of sucralose in waste and surface waters.

Surface waters	
60-80 ng/L	Surface waters (Germany) [1]
<100-1000 ng/L	Rivers in 27 European countries (<100 ng/L in Germany and Eastern Europe)[2]
600 ng/L	Rivers (Switzerland) [2]
nd-1800 ng/L	in 8 surface water samples out of 22 (USA) [3]
600-2400 ng/L	Ground water (USA) [3]
47-2900 ng/L	Source waters of 15 out of 19 WTPs (USA)[4]
up to 300±30 ng/L	Surface waters (AZ, USA)[5]

nd = non-detected.

[1]Scheurer et al. 2009, [2]Buerge et al. 2009, [3]Ferrer and Thurman 2010, [4]Mawhinney et al. 2011, [5]Torres et al. 2011.

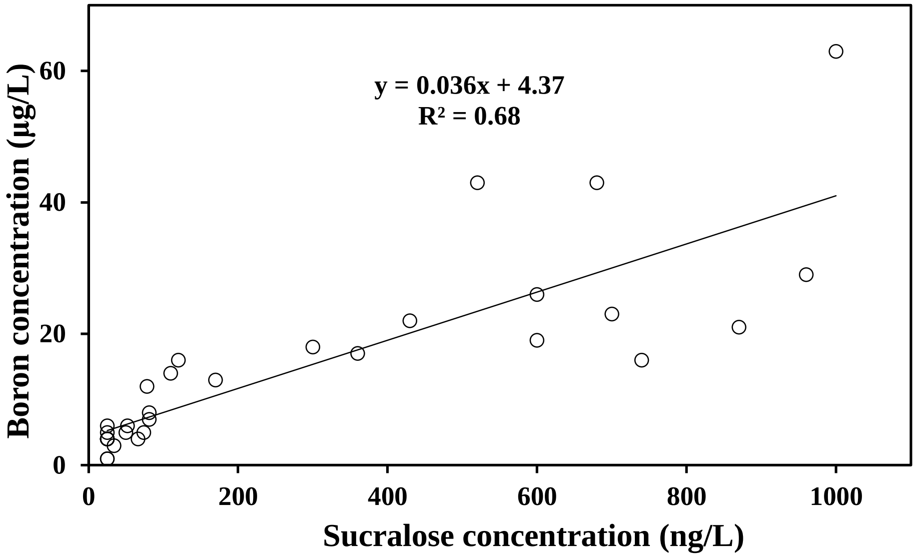


Figure B.1. Linear correlation between boron and sucralose in selected samples.

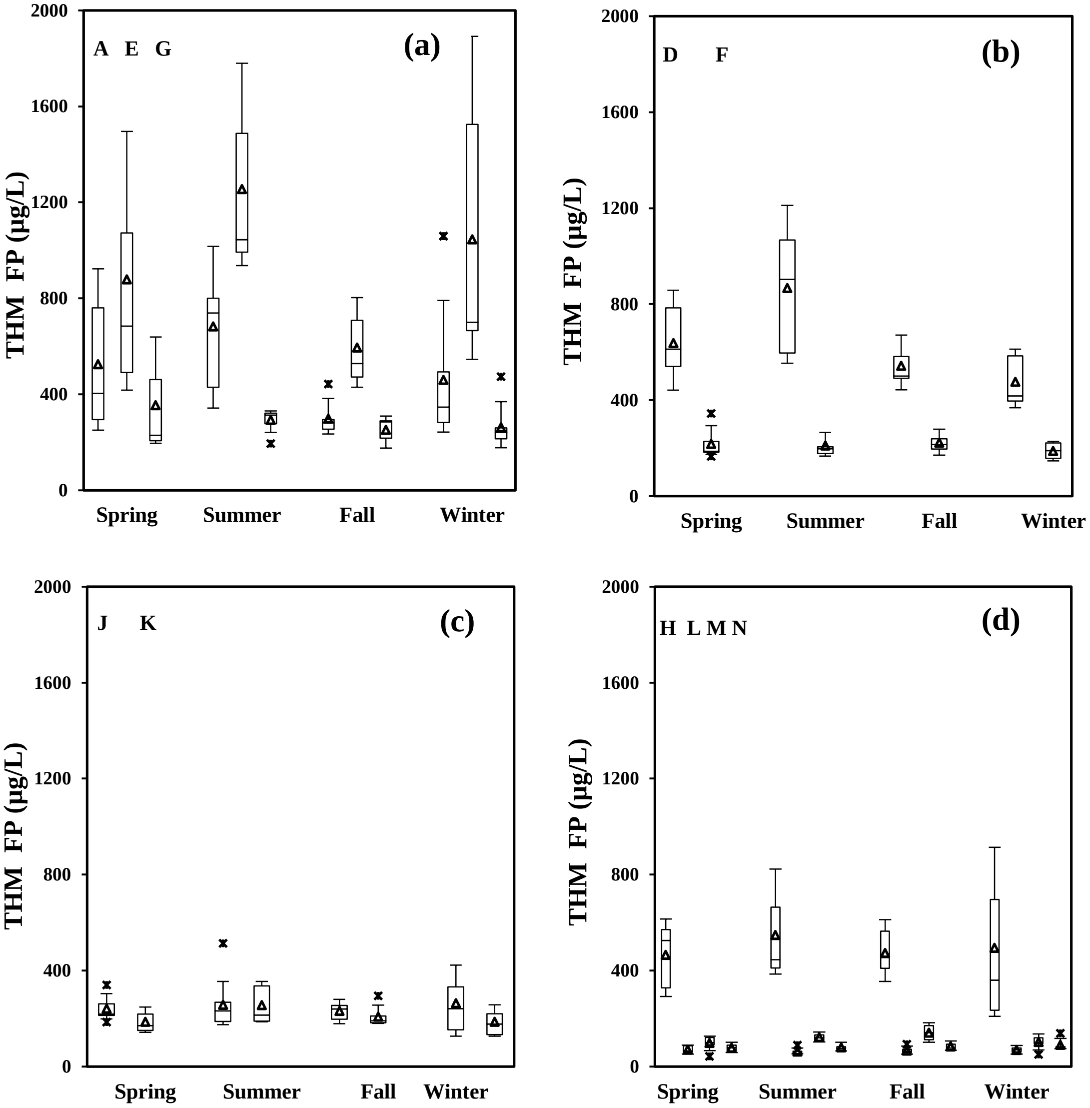


Figure B.2. Seasonal patterns of THM FPs in (a) anthropogenically impacted rivers, (b) anthropogenically impacted lakes/reservoirs, (c) anthropogenically low impacted river and reservoir and (d) limited impacted lakes/reservoirs.

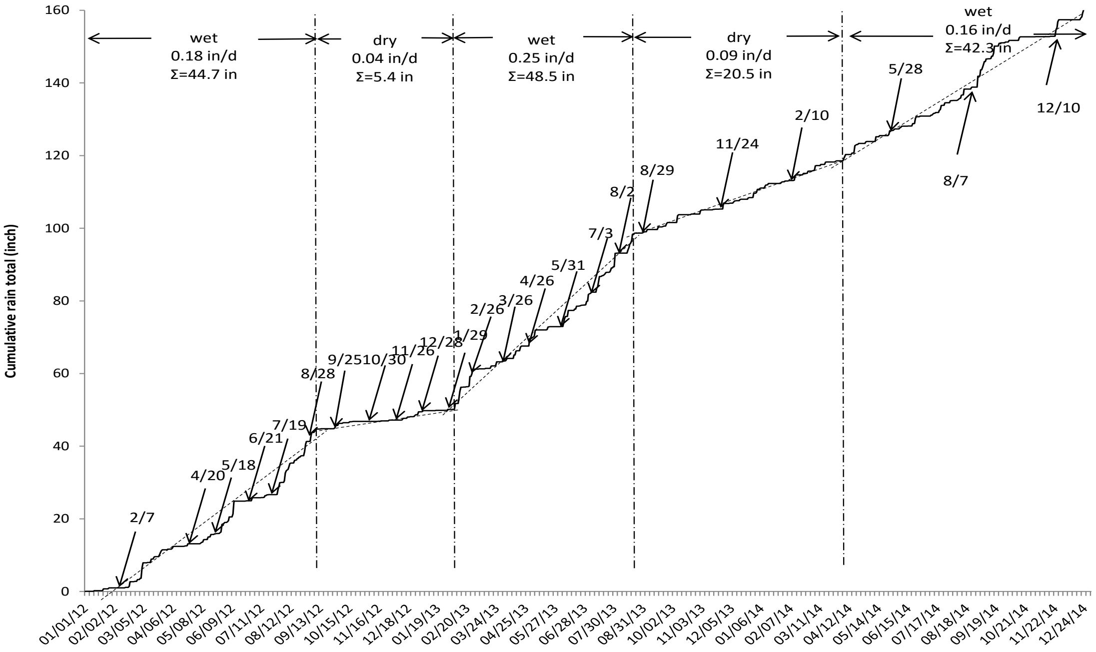


Figure B.3. An example of the cumulative rainfall plot for SW A showing wet and dry rainfall periods.

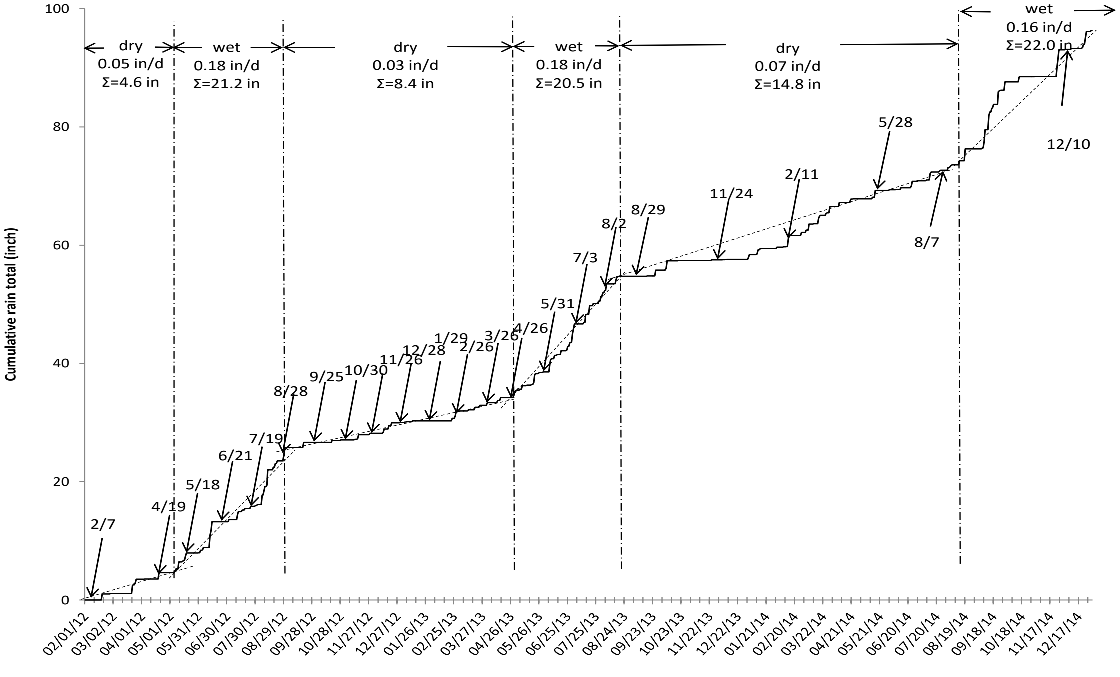


Figure B.4. An example of the cumulative rainfall plot for SW D showing wet and dry rainfall periods.

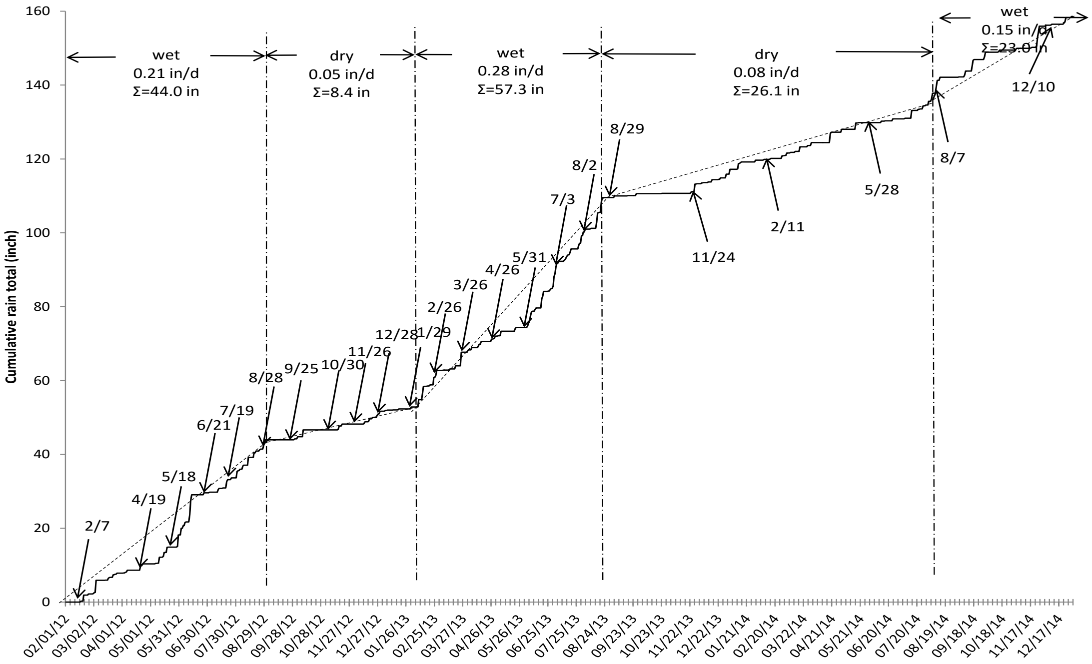


Figure B.5. An example of the cumulative rainfall plot for SW E showing wet and dry rainfall periods.

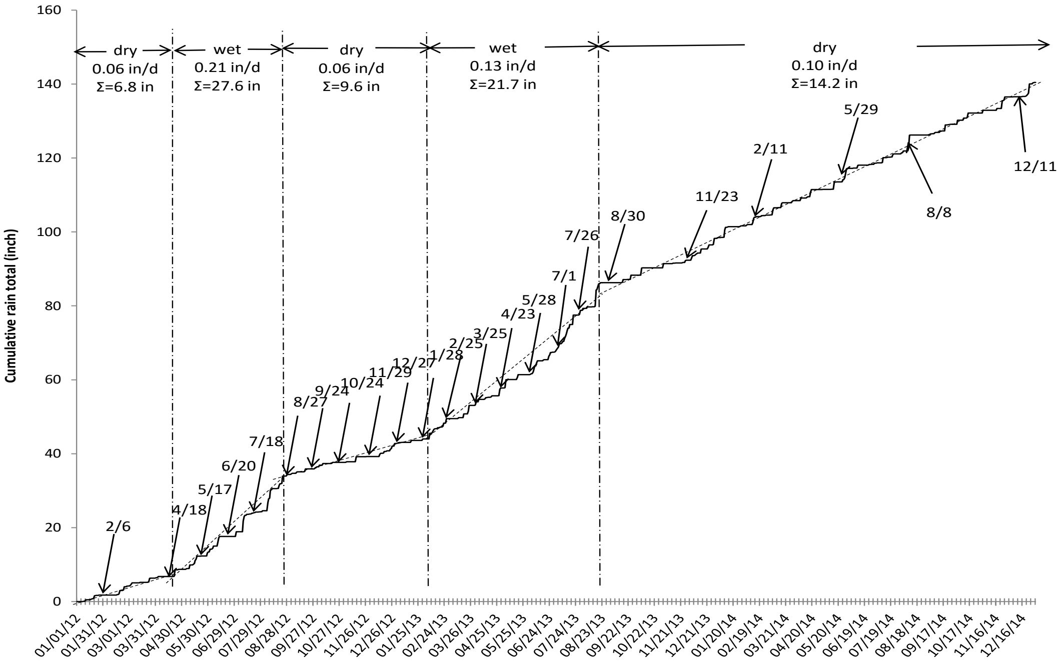


Figure B.6. An example of the cumulative rainfall plot for SW F showing wet and dry rainfall periods.

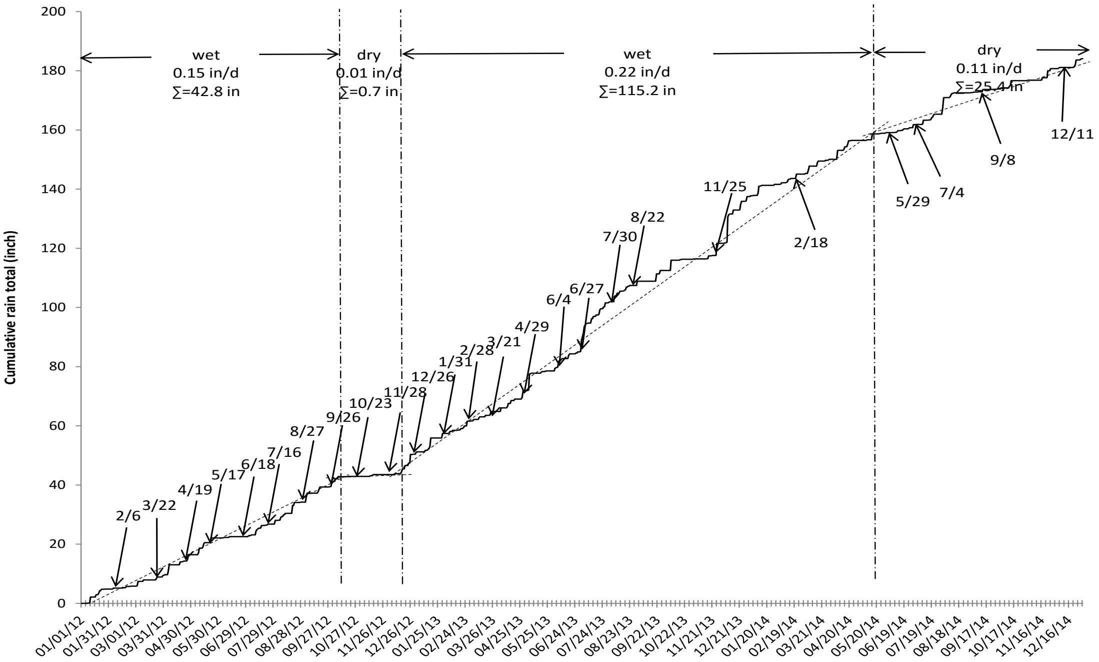


Figure B.7. An example of the cumulative rainfall plot for SW H, SW I, SW J, and SW K showing wet and dry rainfall periods.

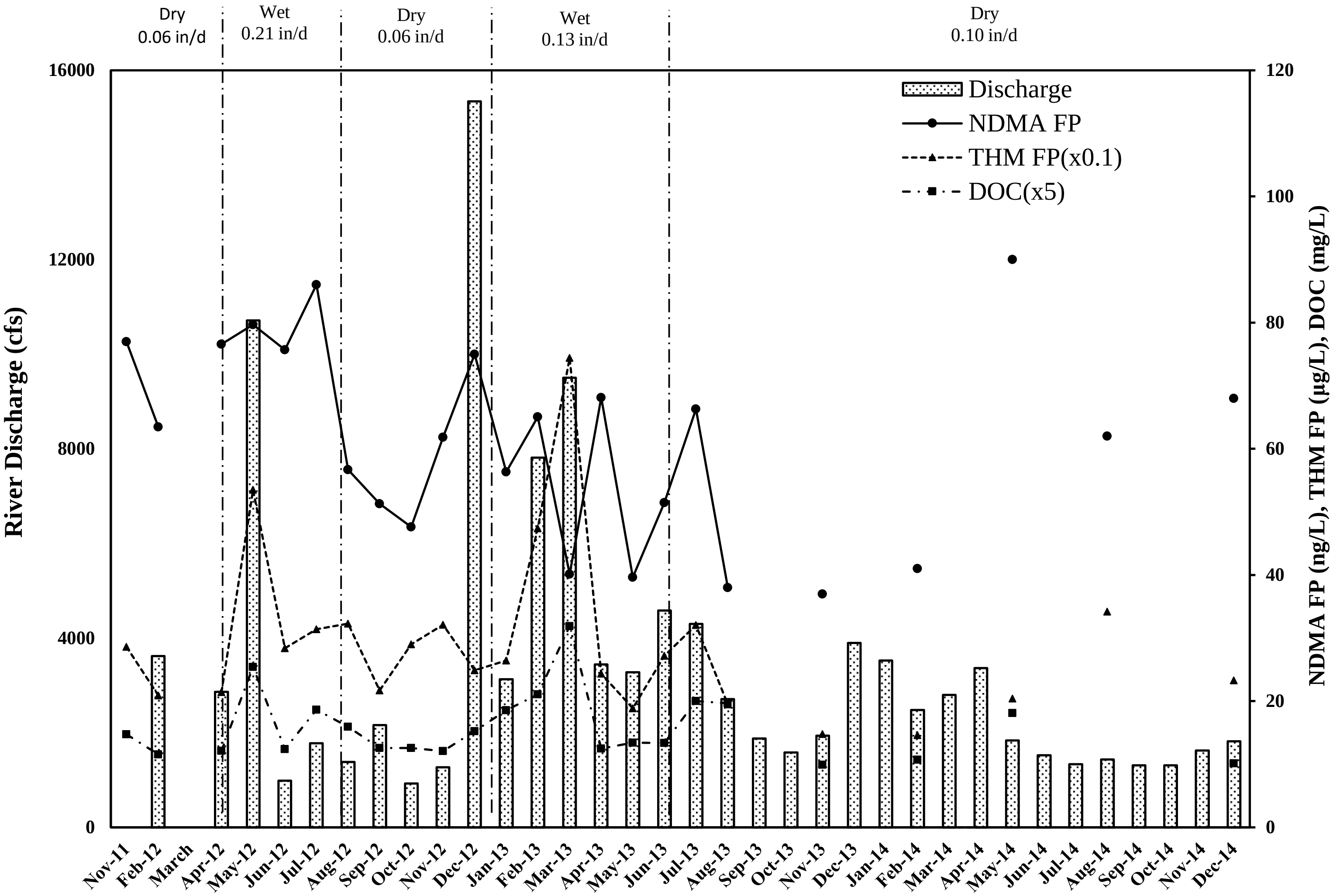


Figure B.8. Observed NDMA FP, THM FP and DOC in the intake of SW G along with monthly average river discharges (cfs).

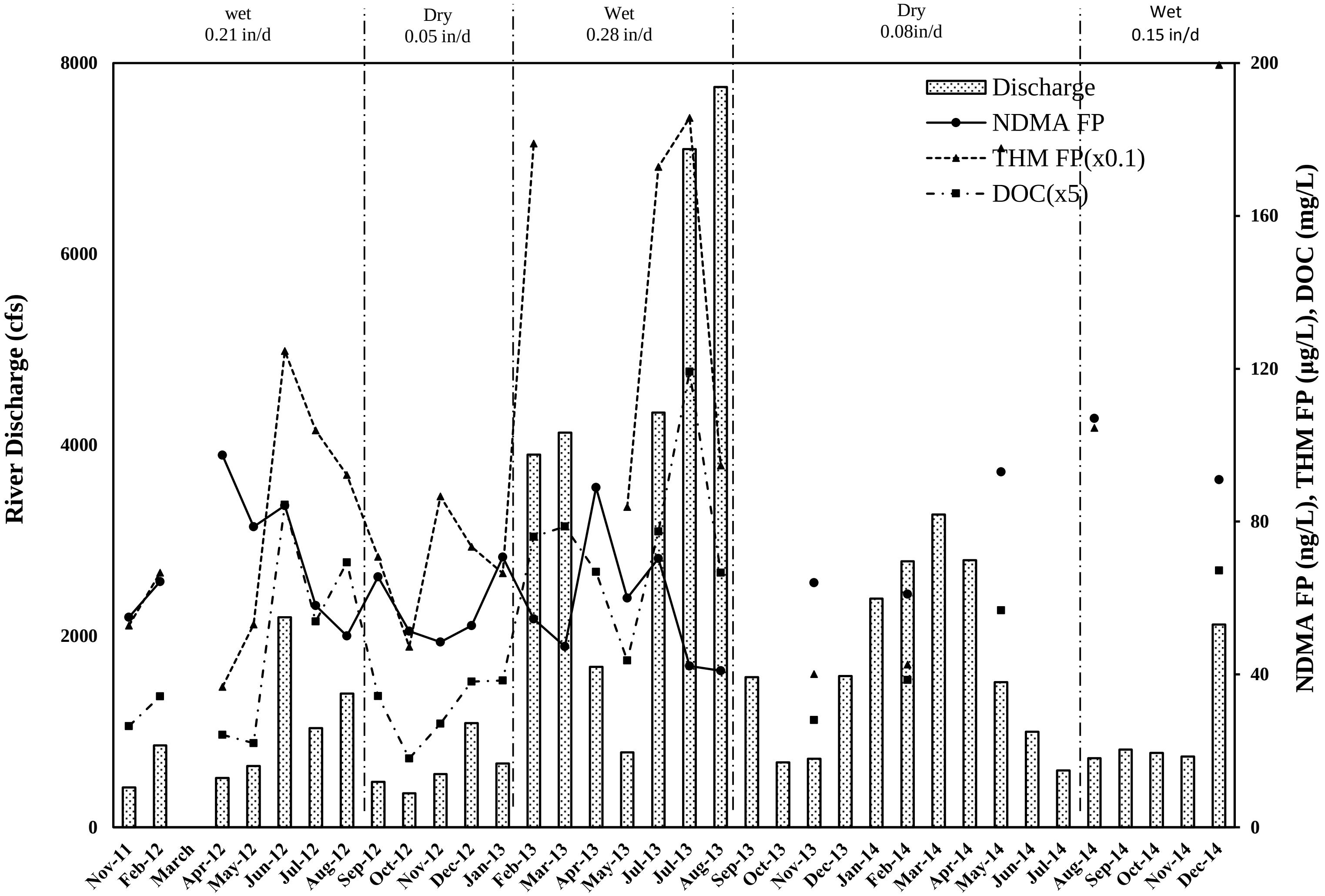
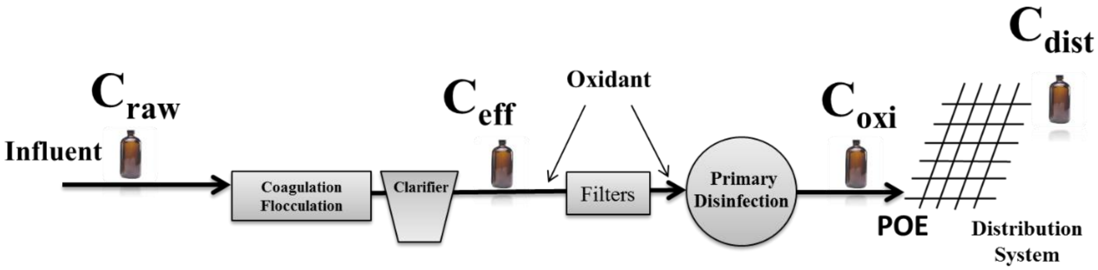


Figure B.9. Observed NDMA FP, THM FP and DOC in the intake of SW E along with monthly average river discharges (cfs).

Appendix C

Supplemental Information for Chapter Six



C_{raw} = Sample in raw water,
$C_{eff.}$ = Sample in treated water (i.e., clarifier effluent, before any oxidant addition),
$C_{oxi.}$ = Sample FP after post oxidation (primary disinfection) (i.e., at POE),
$C_{dist.}$ = Sample in the longest point of the distribution systems.

Figure C.1. Sample collection across water treatment plants.

Table C.1. Median values of nitrosamines' FPs in influent, treated and finished waters.

WTP	NMEA			NDEA			NPYR		
	Plant influent	After clarifier	Finished water	Plant influent	After clarifier	Finished water	Plant influent	After clarifier	Finished water
1	3	4	3	<MRL	<MRL	3	6	4	<MRL
2	3	4	4	3	<MRL	<MRL	8	<MRL	<MRL
3	3	3	3	<MRL	<MRL	<MRL	3	<MRL	<MRL
4	3	<MRL	3	<MRL	<MRL	<MRL	4	<MRL	<MRL
5	4	3	3	6	5	4	4	<MRL	<MRL
6	4	3	4	<MRL	<MRL	<MRL	4	<MRL	<MRL
8	<MRL	4	3	<MRL	<MRL	<MRL	4	4	4
9	3	3	4	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL

WTP	NDBA			NPIP			NDMA		
	Plant influent	After clarifier	Finished water	Plant influent	After clarifier	Finished water	Plant influent	After clarifier	Finished water
1	4	<MRL	<MRL	4	5	5	44	39	25
2	5	<MRL	<MRL	4	3	3	47	36	23
3	<MRL	<MRL	<MRL	3	3	4	43	38	32
4	6	5	5	4	5	6	38	30	22
5	5	<MRL	<MRL	5	7	4	58	28	27
6	3	<MRL	<MRL	7	6	4	31	25	17
8	4	3	<MRL	4	3	ND	25	24	17
9	<MRL	<MRL	3	<MRL	<MRL	<MRL	30	24	18

MRL: Minimum reporting level.

Table C.2. Water quality parameters of raw waters used for polymer experiments.

Waters used	DOC (mg/L)	$SUVA_{254}$ (L/mg-m)	THM FP (µg/L)	NDMA FP (ng/L)
SW A	3.7	2.9	316	34
SW D	5.3	3.4	495	37

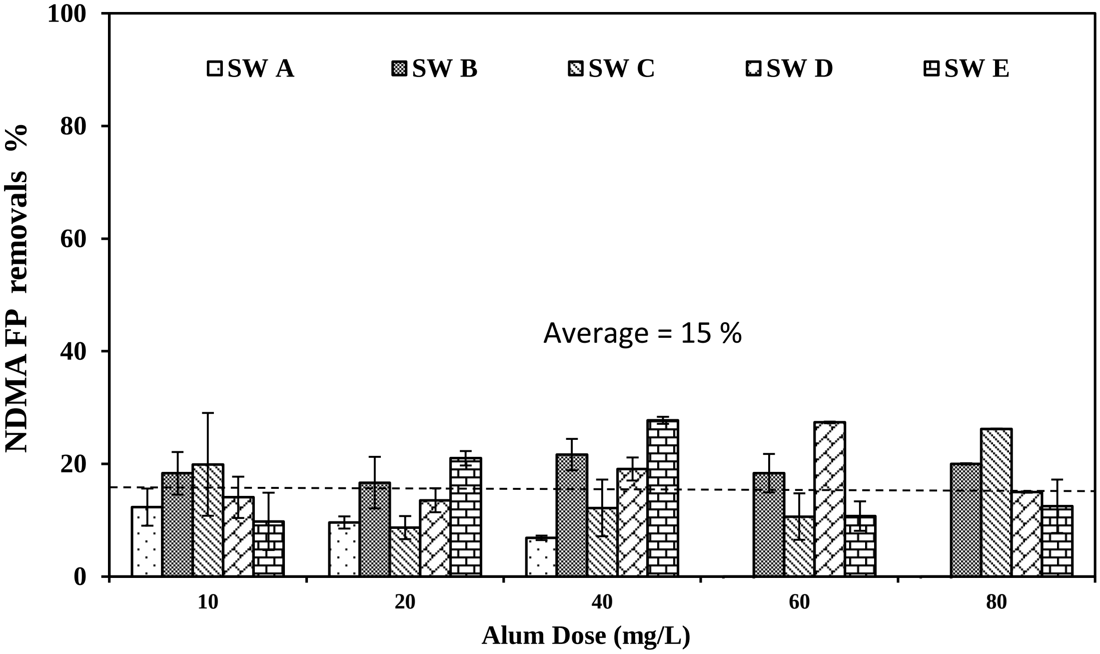


Figure C.2. Removal of NDMA FP from source waters used at WTPs as a function of alum dose (pH ~6). Background waters=SW A, SW B, SW C, SW D and SW E. Alum doses=10, 20, 4, 60 and 80 mg/L, pH ~6. NDMA FP Tests: 100 mg/L NH_2Cl (Cl_2:N=4:1) and contact time= 5 days (pH~7.8). Error bars represent data range for duplicate samples.

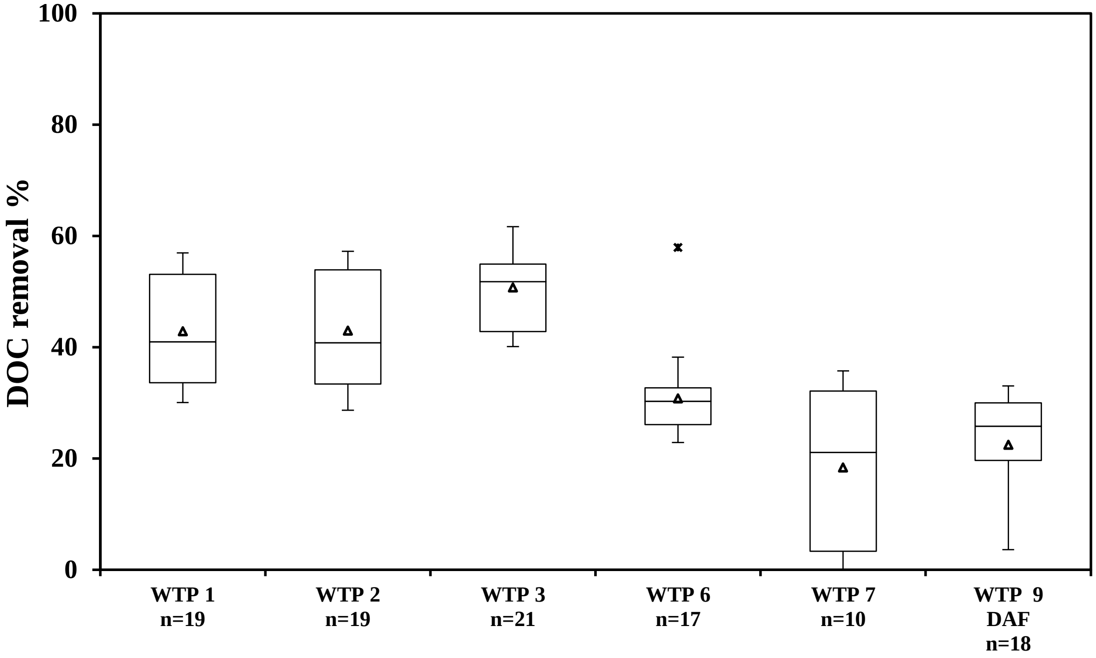


Figure C.3. DOC removals during conventional clarification processes. n denotes # of data.

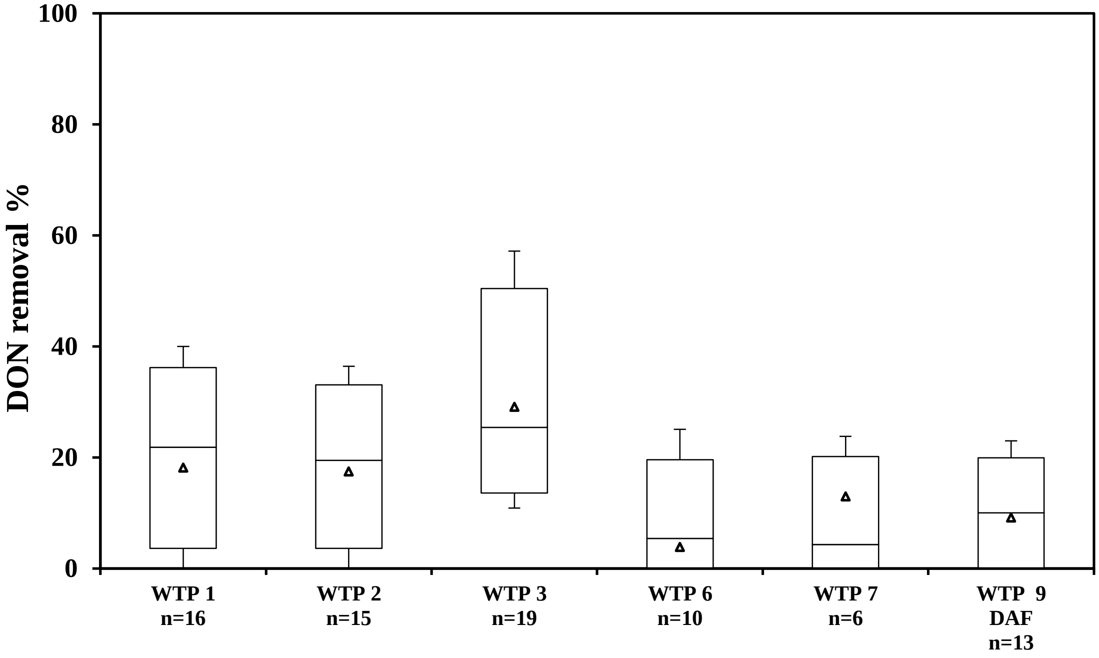


Figure C.4. DON removals during conventional clarification processes**.** n denotes # of data.

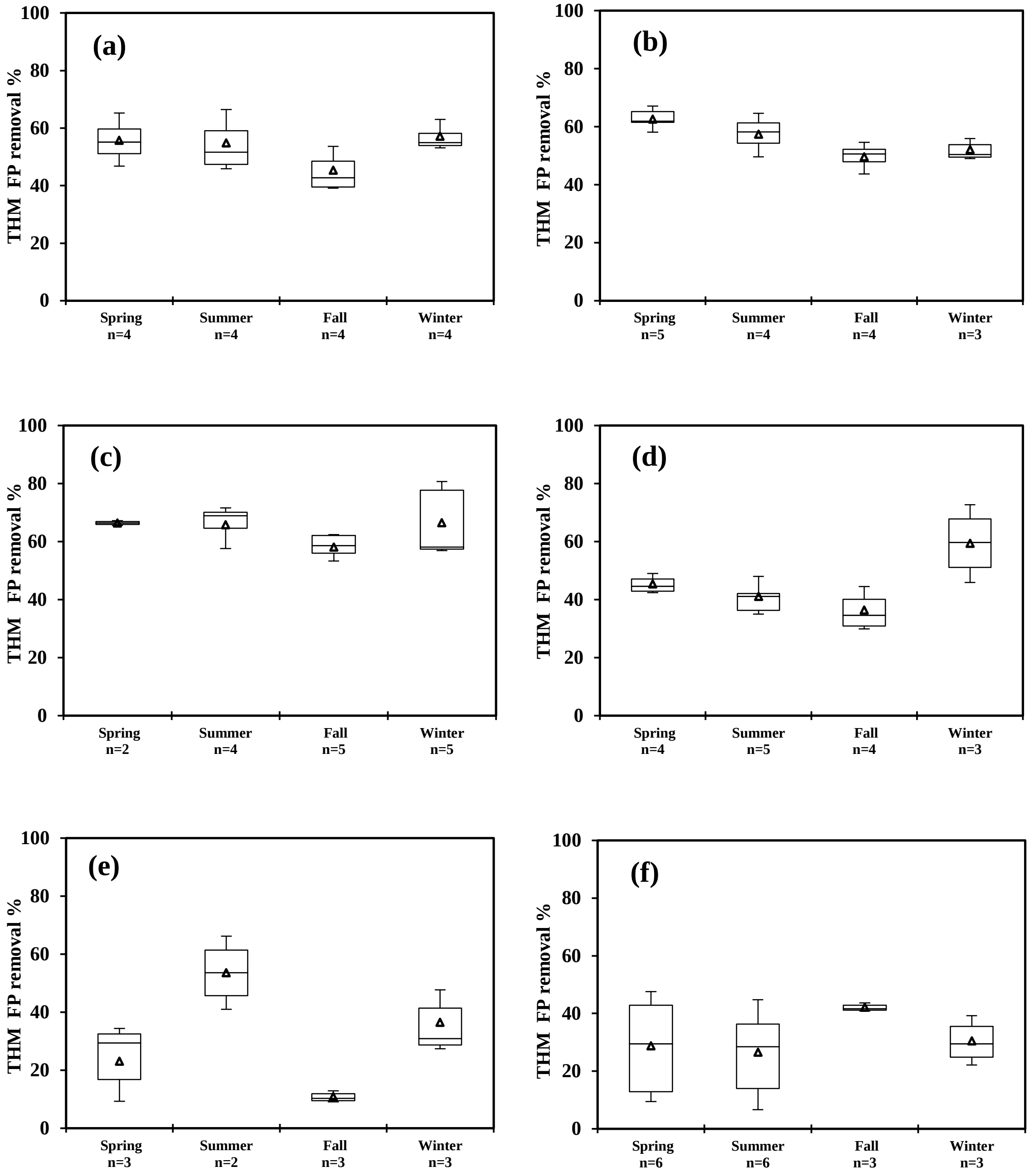


Figure C.5. THM FP removals during different seasons at WTPs (a) 1, (b) 2, (c) 3, (d) 6, (e) 7 and (f) 9. n denotes # of data.

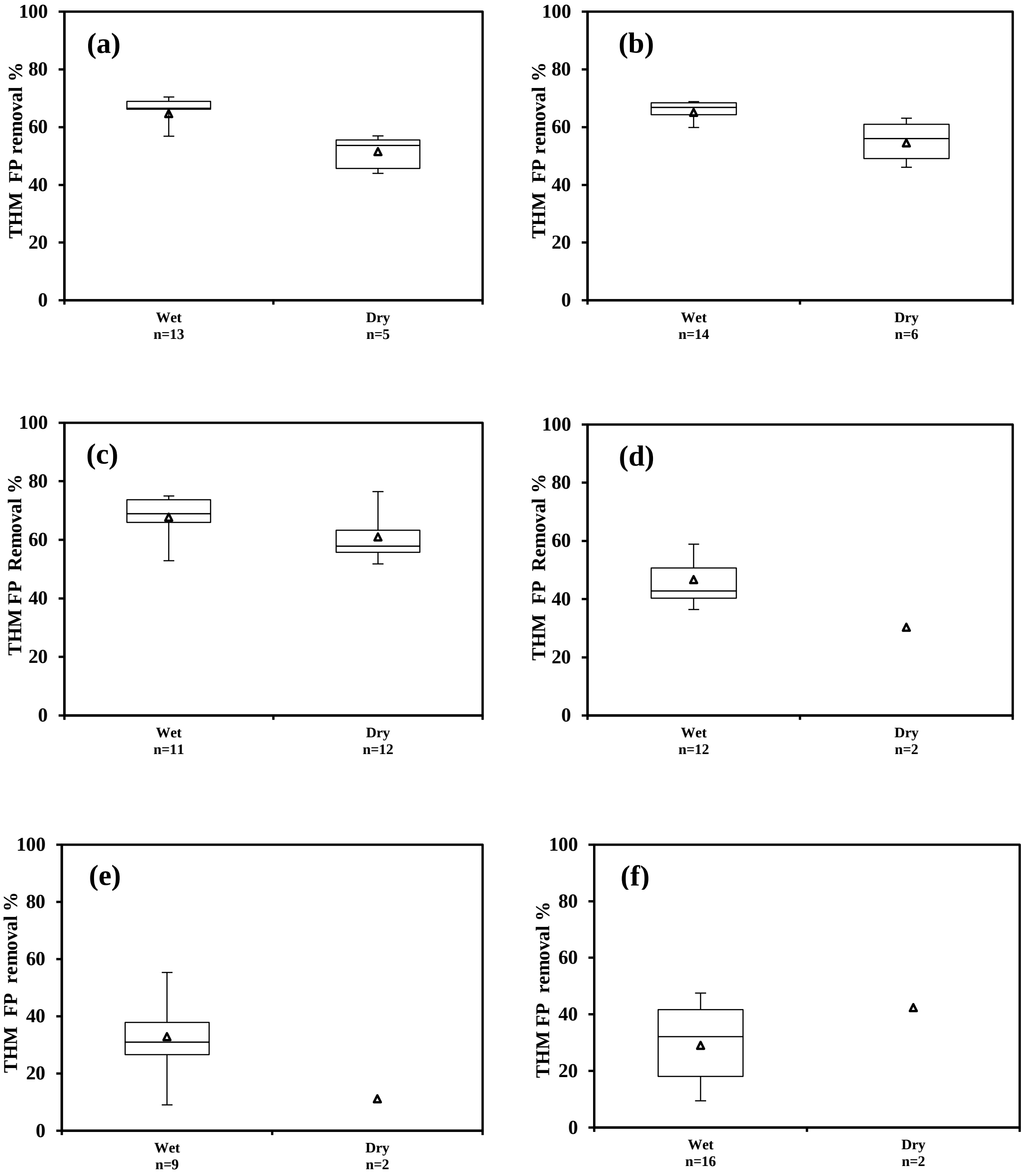


Figure C.6. Comparison of THM FP removal efficiencies at WTPs (a) 1, (b) 2, (c) 3, (d) 6, (e) 7 and (f) 9 during wet (i.e., having rainfalls above the historical regional average 0.13 inch/day) versus dry (i.e., having rainfalls below 0.13 inch/day) rainfall periods. n denotes # of data.

Table C.3. Selected properties of PACs used.

WTP	PAC	Carbon type	BET surface area (m^2/g)	Total pore volume (cm^3/g)	Pore size distribution			*pH_{pzc}
					Micro (%)	Meso (%)	Macro (%)	
2	AquaN	Wood	1727	1.40	23.6	57.5	18.9	5.6
	HD B	Coal	521	0.63	18.7	50.9	30.5	11.3
3	Norit 20B	Coal	1748	1.42	23.0	58.5	18.5	5.4

WTP2 used AquaN one time and HD B two times during the study. WTP3 used Norit 20B six times during the study. *pH_{pzc}: pH at the point of zero charge.

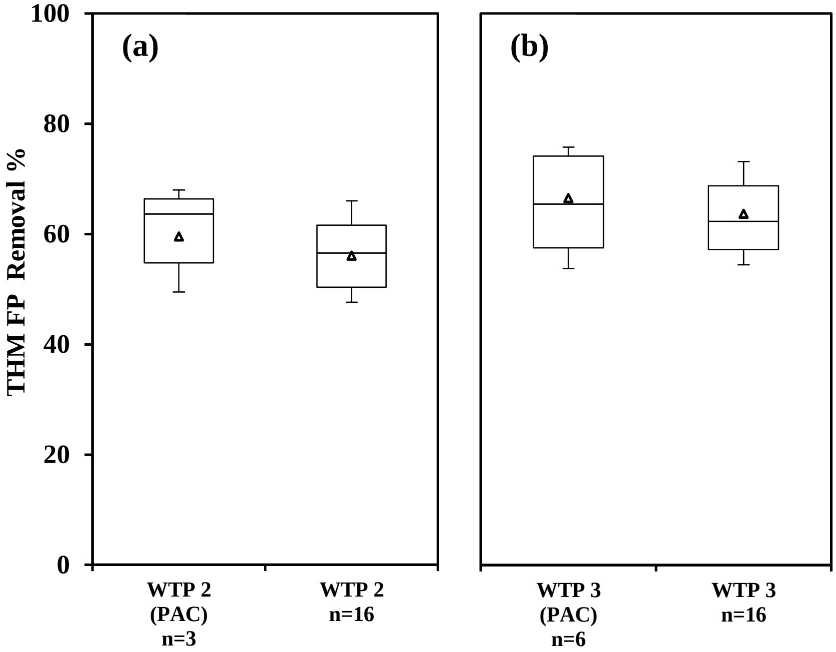


Figure C.7. THM FP removals with and without PAC application at (a) WTP 2 and (b) WTP 3. n denotes # of data.

Table C.4. Average Ct values for post-oxidation with Cl_2

WTPs	$C_{\text{clearwell effluent}}$ (mg/L)	$t_{\text{contact time}}$ (min)	Ct_{applied} (mg*min/L)	Ct_{required} (mg*min/L)	$\frac{Ct_{\text{applied}}}{Ct_{\text{required}}}$	pH
1	2.7	126	355	8	44	7.2
2	2.7	147	373	13	34	7.0
6	1.0	335	332	14	27	6.9
7	1.1	225	245	14	19	7.0
9	2.3	71	160	21	8	7.9

Ct_{required} = Federal requirement for the 0.5 log removal for giardia, and 2 log removal.

Ct_{applied} = Obtained from WTPs during the sampling day.

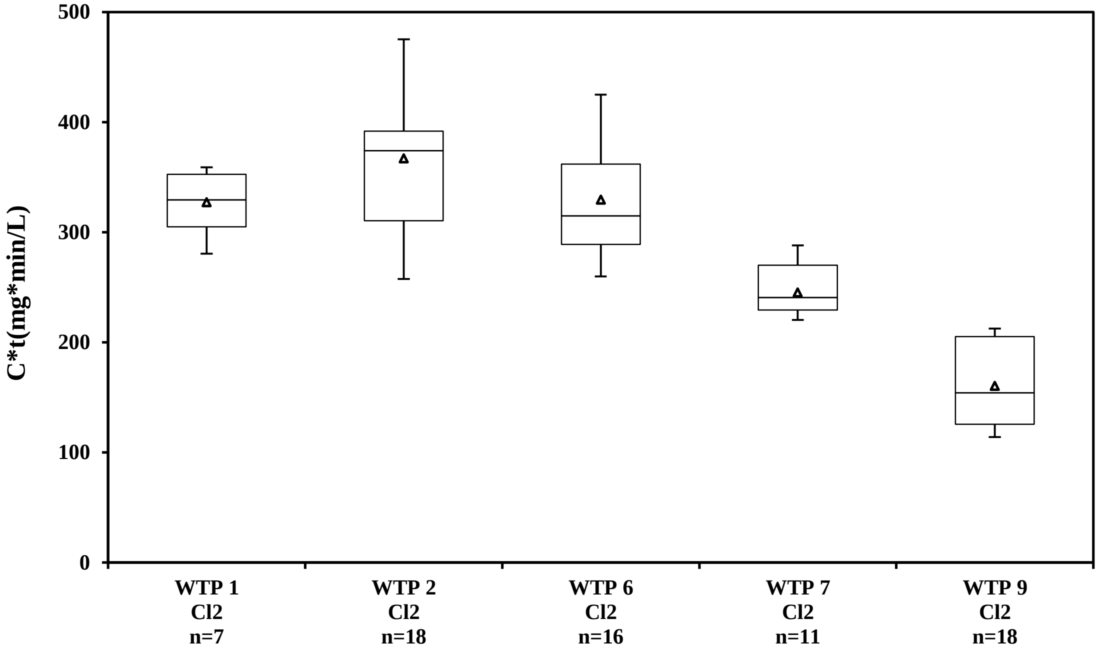


Figure C.8. Ct values of post-oxidation with chlorine only at WTPs without pre-oxidation. n denotes # of data.

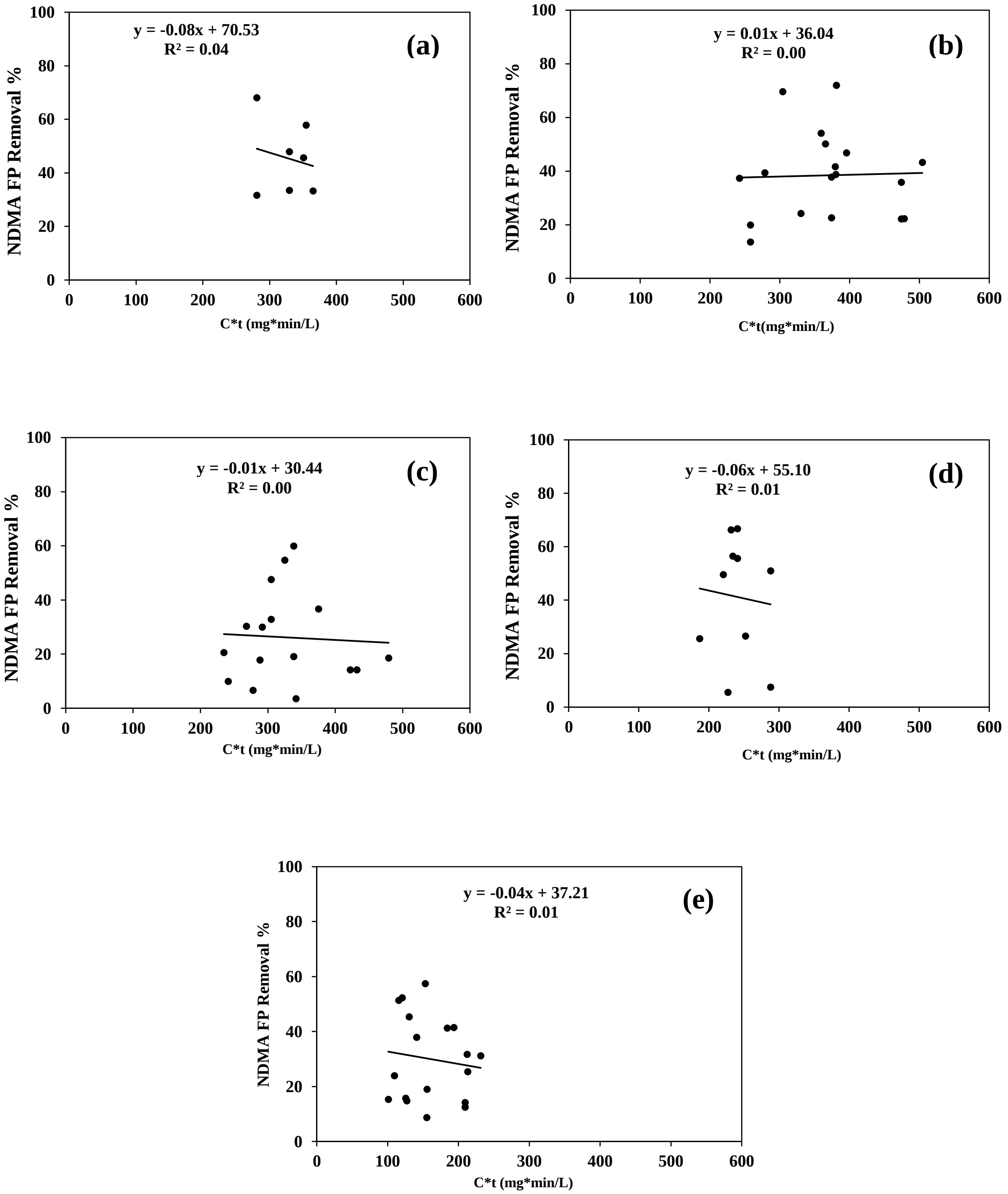


Figure C.9. NDMA FP removal as a function of Ct at WTPs (a) 1, (b) 2, (c) 3, (d) 6, (e) 7 and (f) 9 achieved by chlorine as post-oxidation.

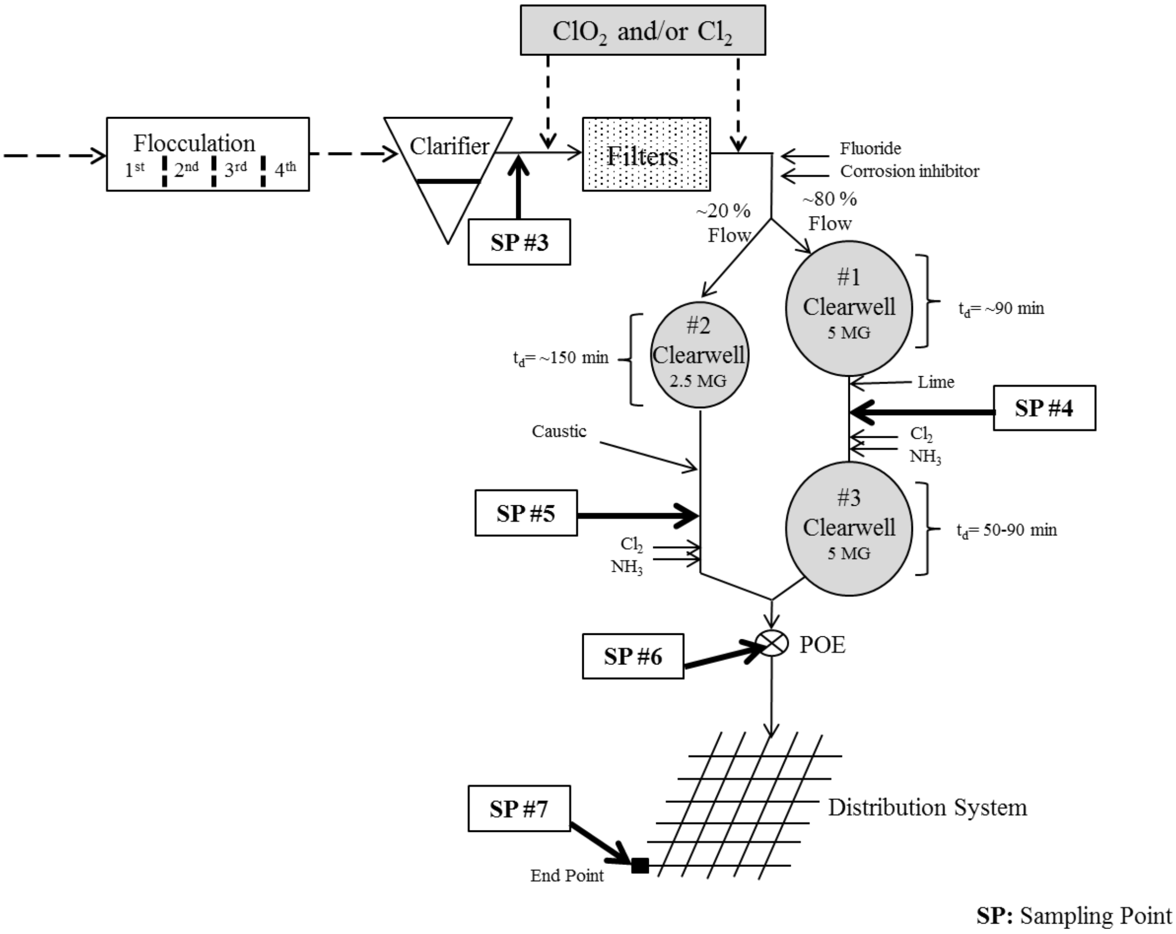


Figure C.10. Disinfection process diagrams and sample collection at WTP 3.

LRAA Calculation

Locational running annual averages (LRAAs) for NDMA occurrences in distribution systems were calculated by taking the average of four consecutive NDMA occurrences as follows:

For example: LRAA of NDMA occurrences in May =

(NDMA in Feb. + NDMA in March + NDMA in April + NDMA in May)/4

Appendix D

Supplemental Information for Chapter Seven

Ct Calculation

Ct (mg*min/L) values were calculated by integrating area under the oxidant residual curve for each target oxidation time as shown in **Figure D.1.** For example, the Ct value for 90 min of oxidation is expressed as the total area under the oxidant concentration curve (i.e., $A_1+A_2+A_3$).

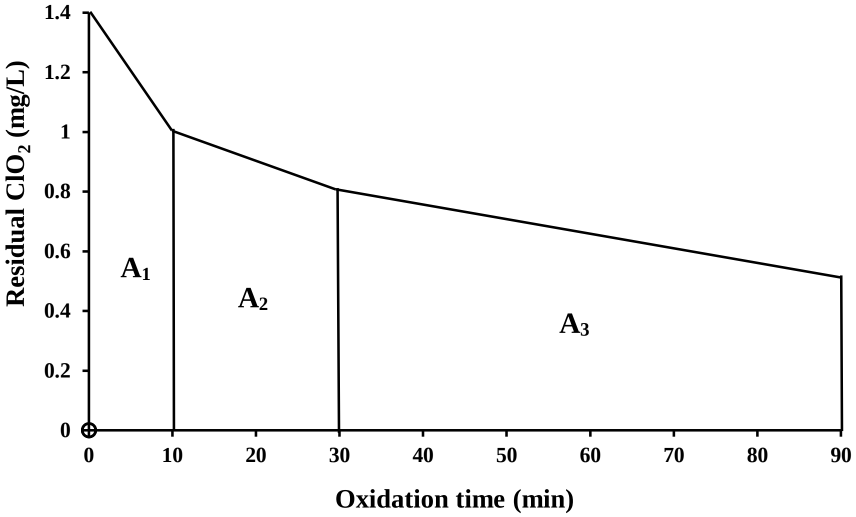


Figure D.1. Ct calculation for the pre-oxidation experiments.

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