



**DOTTORATO DI RICERCA IN INGEGNERIA DELLE  
INFRASTRUTTURE IDRAULICHE, SANITARIO-AMBIENTALI  
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**FORMATION AND CONTROL OF  
N-NITROSODIMETHYLAMINE (NDMA) IN  
WASTEWATER RECLAIMED FOR  
INDIRECT POTABLE REUSE**

**FORMAZIONE E CONTROLLO DI  
N-NITROSODIMETILAMMINA (NDMA)  
IN ACQUE REFLUE DESTINATE AL RIUSO  
POTABILE INDIRETTO**

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*On the cover: West Basin Municipal Water District's wastewater reclamation plant (El Segundo (Los Angeles), California, USA).*

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DESTINATE AL RIUSO POTABILE INDIRETTO)*

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## ABSTRACT

A large diversity of disinfection by-products (DBPs) are formed during water treatment processes using chlorination, including trihalomethanes (THMs) and haloacetic acids (HAAs). Disinfection with chloramines is often used to significantly reduce the formation of regulated DBPs. However, chloramination favours the formation of N-nitrosamines, which are emerging by-products of health and regulatory concern (Mitch et al., 2003). Of all the nitrosamines, N-nitrosodimethylamine (NDMA) has been most commonly detected in drinking water and wastewater (USEPA, 2012) and US Environmental Protection Agency (USEPA) placed it on the drinking water contaminant candidate list 3 (USEPA, 2009). USEPA classifies NDMA as probable human carcinogen, evaluating a  $10^{-6}$  risk level of cancer from NDMA concentration at 0.7 ng/L in drinking water (USEPA, 1987). Nitrosamines can also be produced using alternative disinfectants other than chloramines, including chlorine dioxide ( $\text{ClO}_2$ ) and ozone ( $\text{O}_3$ ) (Najm and Trussel, 2001; Andrzejewski et al., 2008). Particularly, ozone utilization is gaining always more popularity in wastewater treatment for reuse application because of its strong ability to degrade trace organic contaminants (Snyder et al., 2006) and to provide microbial disinfection (Rakness et al., 1993). Nevertheless, wastewater often contains considerable concentrations of NDMA and NDMA precursors (Sedlak et al., 2005; Krasner et al., 2009), and thus, the reuse of treated wastewater for drinking water augmentation, which is emerging worldwide to counter water scarcity, might pose a risk due to the presence of nitrosamines. To date, the NDMA formation mechanisms through the use of different oxidants are not fully understood and all precursors have not yet been identified making the NDMA control challenging during water treatment processes.

The main goals of the present study were: i) to investigate formation and control of NDMA by disinfection and advanced wastewater treatment processes, including chloramination, UV photolysis, reverse osmosis (RO) and advanced oxidation processes (AOPs) (i.e. ozone, UV/hydrogen peroxide ( $\text{H}_2\text{O}_2$ )); ii) to identify the source of NDMA precursors in wastewater; iii) to explore possible NDMA formation

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mechanisms during ozonation also evaluating the possible catalytic effect of inorganic water constituents.

Full scale experiments and lab scale tests were performed using wastewater collected at West Basin wastewater reclamation plant (WWRP) (El Segundo (Los Angeles), California (USA)) and Hyperion wastewater treatment plant (WWTP) (Los Angeles, California (USA)). West Basin WWRP receives wastewater secondary effluent from Hyperion WWTP and it is able to produce through advanced technologies recycled water of quality necessary for potable applications. Wastewaters collected at three WWTPs in Tucson (Arizona (USA)) (Roger Road, Ina Road, Green Valley) were also tested for NDMA formation. Selected experiments were carried out in synthetic water containing NDMA precursors and inorganic constituents (i.e. dimethylamine (DMA), dimethylformamide (DMF), ammonia, bromide).

Obtained results showed that ozonation of wastewater often produced NDMA concentration not in compliance with California's potable reuse requirements (i.e.  $>10$  ng/L) (CDPH, 2009b). Particularly, in Hyperion effluent, under realistic dosages and contact times, a very high and rapid NDMA formation ( $117 - 227$  ng/L) by ozone depended on the applied doses, whereas chloramination or post chloramination has always resulted in far lower amounts of NDMA ( $\sim 20$  ng/L).

Results of this study showed also that RO removes the vast majority of NDMA precursors but it has low effectiveness on NDMA rejection. During UV treatment, the presence of  $H_2O_2$  can reduce NDMA photolysis due to absorption/screening of UV light. Furthermore, UV or UV/ $H_2O_2$  treatment can also enhance NDMA (re)formation during post-chloramination. Likely, it happens because more reactive by-products are formed. However, these effects depend on  $H_2O_2$  concentration and UV dose. Bench scale ultraviolet experiments confirmed an enhanced NDMA formation during chloramination after UV/ $H_2O_2$  treatment of DMF.

Centrates sent back to the head of the treatment plant were identified as the main source of NDMA precursors in Hyperion wastewater. Amino-methylated polyacrilamide (Mannich) polymer used for sludge treatment was the principal cause of NDMA formation. Indeed, its degradable structure released elevated amount of NDMA precursors in the recycle streams. Filtered wastewater samples ( $0.7\ \mu m$ ) produced more NDMA than unfiltered samples confirming that only dissolved compounds reacted with ozone to form NDMA.

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Based on the obtained results, the role of ammonia and bromide on NDMA formation by ozone was investigated. Ozonation of water containing ammonia and bromide leads to the formation of hydroxylamine (HA) and brominated oxidants (e.g. bromamines) that were found to increase the NDMA yield of NDMA precursors such as DMA and DMF. Using DMA as model precursor, new formation pathways were proposed and here reported briefly: ozonation of ammonia and secondary amines forms HA; brominated oxidants are formed in the presence of bromide. DMA reacts with HA and bromine-containing oxidant species to form unsymmetrical dimethylhydrazine (UDMH) or a hypothetical brominated unsymmetrical dimethylhydrazine (UDMH-Br), which subsequently is oxidized by ozone to NDMA. Finally, NDMA formation during ozonation of DMF occurred only in the presence of ammonia and it was attributable to the oxidation of DMF by hydroxyl radicals. Overall, wastewater characterized by elevated ammonia and NDMA precursors load can induce high and rapid NDMA formation by ozone. Therefore, complete biological nitrification may represent an effective treatment method for reducing NDMA formation potential. Furthermore, the presence of bromide can significantly enhance the NDMA formation improving the oxidation of ammonia and amines by ozone and by the subsequent formation of brominated oxidant. During wastewater treatments, RO and UV are used to remove NDMA precursors and degrade NDMA, respectively. Nevertheless, UV or UV/H<sub>2</sub>O<sub>2</sub> treatment may improve the NDMA formation during post-chloramination. Thus, UV dose and the use of H<sub>2</sub>O<sub>2</sub> should be validated also considering the potential NDMA (re)formation during post-chloramination. In addition, the presence of H<sub>2</sub>O<sub>2</sub> can affect the NDMA photolysis. The use of Mannich polymer in sludge treatment should be avoided due to its easily degradable structure that can release elevated amount of NDMA precursors in recycle streams.





## SOMMARIO

L'utilizzo di cloro durante i processi di trattamento delle acque è causa della formazione di diversi sottoprodotti di disinfezione (DBPs), tra cui trialometani (THMs) e acidi aloacetici (HAAs). La disinfezione con cloramine è spesso utilizzata per ridurre la formazione dei DBPs regolamentati. Tuttavia, l'uso di cloramine favorisce la formazione di nitrosammine, sottoprodotti di disinfezione emergenti altamente cancerogeni e d'interesse riguardo a salute pubblica e possibile futura regolamentazione (Mitch et al., 2003). Fra tutte le nitrosammine, la N-Nitrosodimetilammina (NDMA) è la più nota e diffusa in acque reflue e potabili (USEPA, 2012) ed è stata inserita dall'Environmental Protection Agency degli Stati Uniti (USEPA) nella drinking water contaminant candidate list 3 (USEPA, 2009). L'USEPA classifica la NDMA come sostanza probabilmente cancerogena per l'uomo, valutando un livello di rischio di cancro di  $10^{-6}$  per una concentrazione di 0.7 ng/L in acqua potabile (USEPA, 1987). Le nitrosammine possono essere prodotte anche mediante l'utilizzo di disinfettanti alternativi, quali biossido di cloro ( $\text{ClO}_2$ ) e ozono ( $\text{O}_3$ ) (Najm and Trussel, 2001; Andrzejewski et al., 2008). In particolare, l'utilizzo di ozono sta ottenendo sempre una maggiore diffusione nel trattamento delle acque reflue destinate al riuso grazie all'elevata capacità di degradare contaminanti organici in traccia (Snyder et al., 2006) e fornire azione disinfettante (Rakness et al., 1993). Tuttavia, le acque reflue spesso contengono elevate concentrazioni di NDMA e relativi precursori (Sedlak et al., 2005; Krasner et al., 2009) e, dunque, il riuso di acque reflue per applicazioni potabili, il quale sta avendo sempre più diffusione su scala mondiale a causa della crescente e continua scarsità di risorse idriche, potrebbe presentare rischi per la salute pubblica a causa della presenza di nitrosammine in acqua depurata. A oggi, i meccanismi di formazione di NDMA attraverso l'uso di diversi ossidanti non sono completamente noti e tutti precursori non sono stati ancora individuati. Tutto questo causa difficoltà nel controllo e rimozione di tale contaminante durante i processi di trattamento delle acque.

I principali obiettivi del presente studio sono stati: i) investigare la formazione e il controllo di NDMA tramite disinfezione e processi di trat-

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tamento avanzati (cloraminazione, ozonizzazione, osmosi inversa (RO) e processi di ossidazione avanzata (UV/H<sub>2</sub>O<sub>2</sub>)); ii) identificare sorgenti di precursori in acqua reflua; iii) valutare il ruolo di costituenti inorganici nella formazione di NDMA e i possibili meccanismi di formazione.

Sono stati condotti esperimenti a scala reale e di laboratorio utilizzando acque reflue campionate presso l'impianto di depurazione avanzata delle acque reflue West Basin di El Segundo (Los Angeles) (California (USA)) e l'impianto convenzionale di trattamento delle acque reflue Hyperion di Los Angeles (California (USA)). West Basin riceve l'effluente secondario dell'impianto di trattamento Hyperion e attraverso avanzate tecnologie di trattamento è in grado di produrre acqua di qualità necessaria per applicazioni potabili. Acque reflue campionate in tre impianti di trattamento convenzionali di Tucson (Arizona (USA)) sono state anche testate relativamente alla formazione di NDMA tramite ozono. Successivi esperimenti sono stati realizzati in acqua sintetica contenente precursori di NDMA e costituenti inorganici (dimetilammina (DMA), dimetilformammide (DMF), ammoniaca, bromuro).

Questo studio ha mostrato che l'ozonizzazione di acque reflue ha spesso prodotto concentrazioni di NDMA superiori al livello di notificazione per acque potabili dello Stato della California (ovvero, >10 ng/L) (CDPH, 2009b). In particolare, l'effluente di Hyperion è stato caratterizzato da una rapida ed elevata produzione di NDMA tramite ozono (117 – 227 ng/L), mentre la cloraminazione su tempi di contatto e dosi tipiche d'impianti di depurazione ha condotto a un leggero incremento di NDMA (~20 ng/L).

Il processo RO rimuove la maggior parte dei precursori, mentre è inefficace nel rigettare NDMA. Durante il trattamento UV, la presenza di H<sub>2</sub>O<sub>2</sub> può ridurre la fotolisi di NDMA a causa di assorbimento e screening dei raggi UV. Inoltre, il trattamento UV o UV/H<sub>2</sub>O<sub>2</sub> può causare l'aumento della (ri)formazione di NDMA durante una successiva cloraminazione, probabilmente a causa della formazione di sottoprodotti più reattivi. Tuttavia, questi effetti dipendono dalla dose UV utilizzata e dalla concentrazione di H<sub>2</sub>O<sub>2</sub>. Esperimenti a scala di laboratorio hanno mostrato un aumento della formazione di NDMA durante cloraminazione dopo trattamento UV/H<sub>2</sub>O<sub>2</sub> di DMF.

I ricircoli in testa all'impianto provenienti dalla linea fanghi sono stati la principale fonte di precursori di NDMA nell'acqua reflua di Hyperion. Il polimero Mannich utilizzato nella linea trattamento fanghi è stato la causa della presenza di tali precursori. Infatti, la sua struttura chimica facilmen-

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te degradabile ha rilasciato elevate concentrazioni di precursori nei flussi di ricircolo. Campioni di acqua reflua filtrata ( $0.7\ \mu\text{m}$ ) hanno prodotto più NDMA rispetto ai campioni non filtrati confermando che soltanto precursori disciolti hanno reagito con ozono per formare NDMA.

Il ruolo di ammoniaca e bromuro nella formazione di NDMA è stato investigato. L'ossidazione di ammoniaca porta alla formazione d'idrossilammia (HA) e ossidanti bromurati (come ad esempio le bromammine) in presenza di bromuro. Questo studio ha dimostrato che se questi ossidanti sono presenti in acqua, la formazione di NDMA da DMA è significativamente aumentata. Utilizzando DMA come precursore modello i seguenti meccanismi di formazione sono stati proposti: l'ozonizzazione di ammoniaca e ammine secondarie forma HA e ossidanti bromurati in presenza di bromuro. DMA reagisce con HA e specie ossidanti contenenti bromo per formare dimetilidrazina asimmetrica (UDMH) o dimetilidrazina asimmetrica bromurata (UDMH-Br), che è successivamente ossidata dall'ozono formando NDMA. La formazione di NDMA durante ozonizzazione di DMF è avvenuta solo in presenza di ammoniaca ed è attribuibile all'ossidazione di DMF tramite radicali ossidrili.

Complessivamente, acque reflue con alto contenuto di ammoniaca e precursori di NDMA possono essere causa di elevata formazione di NDMA tramite ozono, quindi una completa nitrificazione biologica potrebbe essere un efficace rimedio per ridurre la formazione potenziale di tale composto. La presenza di bromuro può, inoltre, significativamente aumentare la produzione di NDMA durante ozonizzazione a causa della migliorata ossidazione di ammoniaca (il bromuro agisce, infatti, da catalizzatore durante l'ossidazione dell'ammoniaca) e la conseguente formazione di ossidanti bromurati. RO e irraggiamento UV sono utilizzati per rimuovere rispettivamente precursori di NDMA e NDMA. Tuttavia, il trattamento UV/ $\text{H}_2\text{O}_2$  può causare un incremento della formazione di NDMA durante post-cloraminazione; quindi dosi UV e uso di  $\text{H}_2\text{O}_2$  dovrebbero essere validati tenendo anche conto di una potenziale riformazione di NDMA. In aggiunta, la presenza di  $\text{H}_2\text{O}_2$  può influenzare la fotolisi di NDMA. Infine, l'uso del polimero Mannich dovrebbe essere evitato durante il trattamento fanghi a causa dell'elevato rilascio di precursori nei flussi di ricircolo.



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*“L’educazione è l’arma più potente  
che si può usare per cambiare il mondo”*

*“Education is the most powerful  
weapon which you can use to change the world”*

*Nelson Mandela*





# 1 INTRODUCTION

## 1.1 PREMISE

One of the most pervasive problems afflicting people throughout the world is inadequate access to clean water and sanitation. Problems with water are expected to grow worse in the coming decades, with water scarcity occurring globally, even in regions currently considered water-rich (Shannon et al., 2008). The growing global economy and population couple to make water a limited resource in terms of both quantity and quality. The many problems worldwide associated with the lack of clean, fresh water are well known: 1.2 billion people lack access to safe drinking water, 2.6 billion have little or no sanitation, millions of people die annually from diseases transmitted through unsafe water or human excreta (Montgomery and Elimelech, 2007). Water also strongly affects energy and food production, industrial output, and the quality of our environment, affecting the economies of both developing and industrialized nations. Many freshwater aquifers are being contaminated and overdrawn in populous regions – some irreversibly – or suffer saltwater intrusion along coastal regions. With agriculture, livestock and energy consuming more than 80% of all the water for human use, demand for fresh water is expected to increase with population growth, further stressing traditional sources (Shannon et al., 2008).

Thus, reclamation of water after treatment in modern wastewater treatment plants may likely be an important part of sustainable water resource management. Wastewater reuse can be applied for various beneficial purposes such as agricultural irrigation, industrial processes, groundwater recharge, and even for potable water supply after advanced treatment. In this context, studying the fate of contaminants during wastewater treatment is of importance as more and more municipal water treatment

plants are engaged in the practice of intentional or unintentional reuse of the treated wastewater. Particularly, the occurrence of emerging or newly identified contaminants in our water resources is of continued concern for the health and safety of consuming public. Indeed, the existing conventional water treatment plants were not designed for these unidentified contaminants (Bolong et al., 2009).

Nitrosamines are a group of emerging disinfection by-products (DBPs) (Richardson, 2007). They are potent rodent carcinogens and most are classified as probable human carcinogens by the International Agency for Research on Cancer (IARC, 1978). Of all the nitrosamines, N-Nitrosodimethylamine (NDMA) has been most commonly detected in drinking water and wastewater (USEPA, 2012) and it is mutagenic with a life time cancer risk of  $10^{-6}$  for a concentration of 0.7 ng/L (USEPA, 1987). The presence of NDMA is of concern in locations where wastewater effluents are used for potable reuse because disinfection of wastewater effluents may lead to formation of relatively high concentrations of NDMA (Mitch and Sedlak, 2004; Kosaka et al., 2009). Indeed, wastewater often contains significant concentrations of NDMA and other nitrosamines (Sedlak et al., 2005; Krauss et al., 2009) as well as considerable concentration of NDMA precursors (Krasner et al., 2009).

Several studies have shown that NDMA can be generated in water and wastewater treatment system by chlorine-based disinfection process (Choi and Valentine, 2003; Mitch and Sedlak, 2002b; Schreiber and Mitch, 2005; Schreiber and Mitch, 2006a). More recently, researchers have reported that alternative disinfectants including chlorine dioxide ( $\text{ClO}_2$ ) and ozone ( $\text{O}_3$ ) are also able to produce nitrosamines (Najm and Trussel, 2001; Andrzejewski et al., 2007).

To date, there is a knowledge lack about nitrosamine precursor pool and formation mechanisms. Identifying precursors could aid in controlling them at their source. Thus, treatment processes or treatment trains specifically aimed at removing/transforming nitrosamine precursors within water treatment plants or post-formed nitrosamines should be developed.

## 1.2 RESEARCH OBJECTIVES

The overall objective of the present research was to investigate formation and control of NDMA during disinfection and advanced treatments of wastewater destined for indirect potable reuse. Specific objectives were:

- ✓ to evaluate NDMA formation during ozonation of wastewaters of different characteristics;
- ✓ to compare NDMA formation in wastewater during ozonation and chloramination upon dosages and contacts times typical of wastewater treatment plants;
- ✓ to determine the effect of different UV doses and  $\text{H}_2\text{O}_2$  on NDMA photolysis and (re)formation during post-chloramination;
- ✓ to identify the source of NDMA precursors within a wastewater treatment plant by ozonation;
- ✓ to investigate the effect of ammonia and bromide on NDMA formation during ozonation and the possible formation mechanisms.

## 1.3 ORGANIZATION OF THE WORK

This dissertation includes five chapters. Following this introduction, chapter 2 illustrates background information on wastewater reuse and general information on the DBP N-Nitrosodimethylamine (NDMA). Particularly, the reported information is focused on physical and chemical properties, health concerns and exposure, occurrence and regulation, formation mechanisms and known precursors of NDMA. Effective technologies for NDMA precursors and NDMA removal are also described. The information on materials and methods used in this research is described in chapter 3. Experimental results concerning the NDMA formation along advanced wastewater treatment processes by chloramination are described in chapter 4. In this chapter, results related to NDMA formation upon ozonation, precursors source investigation and ammonia and bromide role on formation mechanisms of NDMA are also discussed. Finally, the conclusions are presented in chapter 5.



## 2 BACKGROUND INFORMATION

This chapter presents background information concerning the emerging disinfection by-product (DBP) N-Nitrosodimethylamine (NDMA). In particular, health concern and exposure, occurrence and regulation, formation mechanisms, precursors and removal are described. First, the water reuse context and an overview of the common treatments used in an indirect potable reuse system are presented.

### 2.1 WATER REUSE

The overarching goal for the reclamation and re-use of water is to capture water directly from non traditional sources such as industrial or municipal wastewaters and restore it to water of different quality depending on the ultimate use of that resource.

As previously mentioned, wastewater reuse can be applied for various beneficial purposes such as agricultural irrigation, industrial processes, groundwater recharge, and even for potable water supply after extended treatment. To ensure sustainable and successful wastewater reuse applications, the following requirements must be fulfilled:

- ✓ the potential public health risk associated with wastewater reuse need to be evaluated and minimized;
- ✓ the specific water reuse applications must meet the water quality objectives.

Municipal wastewaters are commonly treated by activated sludge systems that use suspended microbes to remove organics and nutrients, and large sedimentation tanks to separate the solid and liquid fractions. This level of treatment produces wastewater effluent suitable for discharge to surface waters or for restricted irrigation and some industrial application (Shannon et al., 2008).

Nowadays, several countries in the world use to treat wastewater for potable reuse. It is possible to distinguish:

- ✓ direct potable reuse, when purified recycled water is added directly to the potable or drinking water supply;

- ✓ indirect potable reuse (IPR), when the purified recycled water is pumped into an underground aquifer or a dam. It then mixes with the water already present and the mixed water is pumped out and treated for the potable drinking water supply.

For water reuse in the U.S.A., States can refer to the U.S. EPA *Guidelines for Water Reuse* (USEPA, 2004), California's Department of Public Health (CDPH) Title 22 requirements (CDPH, 2009a), or local standards for wastewater contaminants. In 2004, only four States (California, Florida, Hawaii, and Washington) had specific standards for IPR, and they generally addressed total suspended solids (TSS), total nitrogen (TN), total organic carbon (TOC), turbidity, total organic halides (TOX), and total coliforms. Wastewater intended for IPR is also expected to comply with drinking water standards.

Recently, public attention was also addressed to de facto wastewater reuse, i.e. the unplanned or incidental presence of treated wastewater in a water supply source. It is not uncommon for a substantial portion of the source water for drinking water treatment plants (DWTPs) to be originally derived from upstream treated wastewater contributions to the surface water resource. An EPA study of the 1980 realized by Swayne et al. (1980) estimated approximately 4 million of the 62 million people served by surface water supplies in the United States were using wastewater-impacted water supplies. Rice et al. (2013) provided an update of the study of Swayne et al. (1980) reporting an increased de facto reuse from 1980 to 2008 for 17 of the top 25 most impacted DWTPs identified in the EPA study, as the municipal flows upstream of the sites increased by 68%. This study also reported that under low stream flow conditions, de facto reuse in DWTP supplies ranged from 7% to 100%, illustrating the importance of wastewater in sustainable water supplies.

In this context, studying the occurrence and fate of emerging or newly identified contaminants during water treatments presents many challenges concerning the health and safety of consuming public.

## 2.2 WATER TREATMENTS FOR POTABLE REUSE

Typical IPR system comprises membrane treatments, including microfiltration (MF) and reverse osmosis (RO), advanced oxidation processes (AOPs), and final disinfection. This train of treatment is also indicated

from different international guidelines as suitable for IPR (USEPA, 2004; Australia, 2008; CDPH, 2009a). In this section an overview of the common treatments used in an IPR system is presented. Their properties and efficacy are briefly discussed.

### 2.2.1 Membrane processes

A membrane process can be defined as an operation where a feed stream is divided into two streams: a permeate containing material which has passed through the membrane and a retentate or concentrate containing the nonpermeating species. Membrane processes can be used to concentrate or to purify a solution or a suspension (solvent-solute or particle separation) and to fractionate a mixture (solute-solute separation). There are membrane processes in which the driving force is a pressure difference across the membrane. It is possible to distinguish:

- ✓ Reverse Osmosis (RO). RO is a pressure-driven membrane operation in which the solvent of the solution is transferred through a dense membrane tailored to retain salts and low-molecular-weight solutes. If a concentrated saline solution is separated from pure water by such a membrane, the difference in chemical potential tends to promote the diffusion of water from the diluted compartment to the concentrate compartment in order to equalize the concentrations. At equilibrium, the difference in the levels between the two compartments corresponds to the osmotic pressure of the saline solution. To produce “pure” water from a saline solution, the osmotic pressure of the solution must be exceeded in the brine.
- ✓ Nanofiltration (NF). NF, also called low-pressure reverse osmosis or membrane softening, lies between RO and ultrafiltration in terms of selectivity of the membrane which is designed for removal of multivalent ions (calcium and magnesium) in softening operations. More recently, NF has been employed for organics control. In NF, the monovalent ions are poorly rejected by the membrane. This explains why NF leads to an osmotic back-pressure which is much lower than that experienced with RO. As a consequence, the operating pressure used in NF is much lower than in RO.
- ✓ Ultrafiltration (UF). In water treatment, UF can be defined as a clarification and disinfection membrane operation. UF mem-

branes are porous and allow only the coarsest solutes (macromolecules) to be rejected, and, a fortiori, all types of microorganisms as virus and bacteria, or all types of particles. Since the low-molecular-weight solutes are not retained by UF, the osmotic backpressure can be neglected, and the operating pressure is kept low.

- ✓ Microfiltration (MF). A major difference between MF and UF is membrane pore size; those of MF are 0.1  $\mu\text{m}$  or greater. The primary application for this operation is particulate removal (clarification). Pressures are similar to UF.

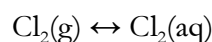
As materials accumulate near, on, and within the membrane, they may reduce the permeability of the membrane by blocking or constricting pores and by forming a layer of additional resistance to flow across the membrane. Decreases in permeate flux decline are referred to as membrane fouling. Washing the membrane, either hydraulically or chemically, may remove some of the accumulated materials and partially restore permeate flux.

### 2.2.2 Chlorination

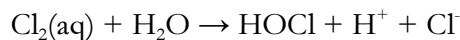
Chlorination of potable water supplies was first initiated in the early years of the 20th century. Chlorine is still the most widely used disinfectant in the world because it is very effective against a wide range of pathogens including bacteria and viruses; it is stable and therefore capable of providing the necessary residual protection in the distribution system. Moreover it is the most economical disinfection technique.

Chlorine is usually supplied in water treatment as gas (molecular chlorine), aqueous hypochlorite solution (sodium hypochlorite,  $\text{NaOCl}$ ) or dissolved solid (calcium hypochlorite,  $\text{Ca(OCl)}_2$ ).

Molecular chlorine is a gas at normal temperatures and pressures. Although dissolution of the gas into an aqueous solution initially generates  $\text{Cl}_2(\text{aq})$ , that species is unstable at near-neutral pH and disproportionates rapidly (with a characteristic reaction time on the order of 0.08 s) to form equal concentrations of hydrochloric acid ( $\text{HCl}$ ) and hypochlorous acid ( $\text{HOCl}$ ).  $\text{HCl}$  is a strong acid that dissociates completely, whereas  $\text{HOCl}$  is a weak acid ( $\text{pK}_a = 7.5$ ) that dissociates only partially, according to the following reactions (Stumm and Morgan, 1996; MWH, 2005):

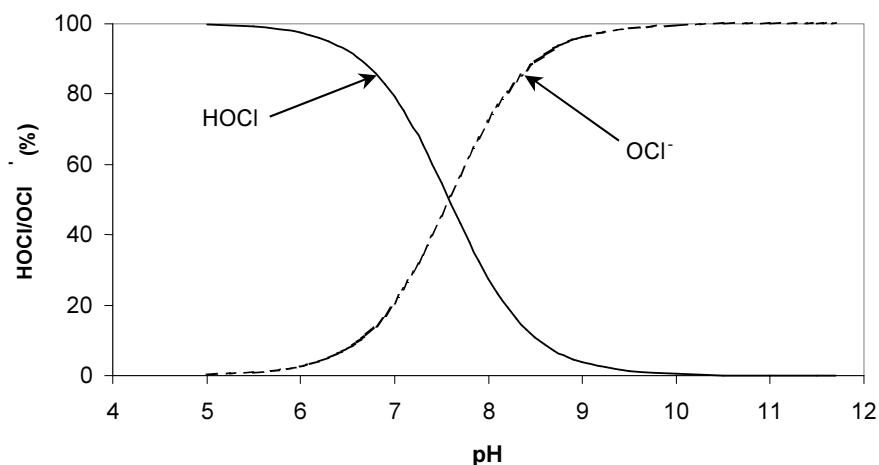






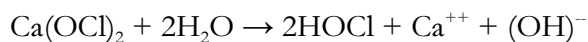
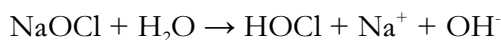
Both hypochlorous acid and hypochlorite anion are good oxidants, with HOCl recognized to be the much more facile oxidant of the two. HOCl and  $\text{OCl}^-$  are collectively referred to as free chlorine or free available chlorine (FAC), however the free chlorine is reported as  $\text{Cl}_2$ .

The relative amount of HOCl and  $\text{OCl}^-$  is a function of pH. In particular, in water of pH between 6.5 and 8.5 both species are present to some degree according to the diagram shown in Figure 2.1.



**Figure 2.1** Speciation of hypochlorous acid

On the other hand, sodium hypochlorite and calcium hypochlorite hydrolyze in water according to the following reactions:

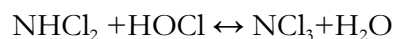
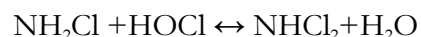
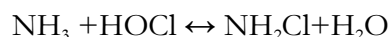


### 2.2.3 Chloramination

Chloramination of drinking water has been practiced in the United States for nearly 80 years for the purposes of both disinfection and taste and odor control. In the last decades its application in drinking water treat-

ment plants (DWTPs) increased in the USA in order to reduce disinfection by-products (DBPs) formation and particularly trihalomethanes (THMs) formation (U.S. EPA, 1999a). However, formation of other emerging DBPs was found out, particularly nitrogen containing DBPs that are often more genotoxic, cytotoxic, or carcinogenic (Shah and Mitch, 2012). Furthermore, in MF/RO treatment for water reuse applications, it is standard practice to chloramine wastewater before MF to minimize RO membrane fouling (Bartels et al., 2005).

In the presence of ammonia, free chlorine (HOCl) reacts rapidly and in a stepwise manner to form mono- ( $\text{NH}_2\text{Cl}$ ), di- ( $\text{NHCl}_2$ ), and trichloramine referred also as nitrogen trichloride ( $\text{NCl}_3$ ), according to the following reactions (Metcalf & Eddy, 2003; MWH, 2005):



The dominant chloramine species that forms in a given solution depends on pH, the chlorine to ammonia ratio, the temperature, and the contact time. Trichloramine is not important under most conditions of interest due to either the preferential formation of the other forms and/or its instability reactions (U.S. EPA, 1999).

In the absence of other rapidly reacting, Cl-consuming substances, the behaviour of the chloramines is mostly dependent on the  $\text{Cl}_2:\text{N}$  molar ratio, but other solution characteristics (particularly pH and the presence of acid anions) also have noticeable effects. In general, when this ratio is less than 1, virtually all of the free chlorine is consumed and monochloramine is the dominant species formed reactions (U.S. EPA, 1999).

Monochloramine is the preferred chloramine species for use in water treatment not only because of efficacy, but because the taste and odor problems associated with dichloramine and nitrogen trichloride are more severe.

Chloramines are not as strong as other chemical disinfectants, such as chlorine, ozone, and chlorine dioxide. They are effective as a disinfectant against bacteria in water, but they are weaker disinfectants compared to

chlorine especially for virus and protozoa inactivation. Chloramines are very stable and provide a residual protection in the distribution system.

#### 2.2.4 Ozonation

Ozone was first used for drinking water disinfection in Europe in the late 19<sup>th</sup> century. Today ozone is used for the treatment of drinking waters, wastewaters, cooling waters, swimming pools, and aquaria.

Ozone is the strongest commercially available oxidizing agent. It is an excellent disinfectant and can even be used to inactivate microorganisms such as protozoa which are very resistant to conventional disinfectants. Other important goals of ozonation are improvement of taste, reduction of color and odor, oxidation of iron and manganese, enhancement in biodegradability of organic compounds, and improvement in flocculation and filtration performance (U.S. EPA, 1999).

In addition, ozone utilization is gaining always more popularity in water reuse applications because of its strong dual ability to degrade trace organic contaminants (Snyder et al., 2006) and to provide microbial disinfection in wastewater (Rakness et al., 1993). In addition, ozonation can also be used to reduce organic fouling on (RO) membranes due to the transformation of organic matter (Standford et al., 2011). Since RO is an energy intensive process, pre-ozonation has the potential to yield sufficient energy and cost saving to warrant its inclusion in advanced treatment trains (Pisarenko et al., 2012).

At room temperature, ozone exists as a colorless gas with a pungent odor that is readily detectable at concentrations as low as 0.02 to 0.05 ppm (by volume). Ozone is sparingly soluble in water. At 25°C, ozone is less volatile (i.e., more soluble) than oxygen, but significantly more volatile than chlorine. When ozone is used in water treatment, its gas-phase mole fraction is typically less than 14 percent; as a result, the mass transfer driving force is limited, with the result that dissolved ozone concentrations greater than about 2-3 mg/L are difficult to achieve without significant optimization (U.S. EPA, 1999).

Some ozone also reacts with hydroxide ions to produce molecular oxygen and the hydroperoxy anion ( $\text{HO}_2^-$ ), the conjugate base of hydrogen peroxide ( $\text{H}_2\text{O}_2$ ). The latter product can react further with ozone to produce two free radicals: the uncharged hydroxyl radical ( $\bullet\text{OH}$ ), which can be thought of as a hydroxyl ion from which an electron has been abstracted and the superoxide anion ( $\text{O}_2^-\bullet$ ), which can be thought of as an

oxygen molecule to which an electron has bound. The net result of these reactions is the conversion of two molecules of ozone and one hydroxide ion into two molecules of oxygen and the two free radicals. The rate at which ozone decays via this pathway increases dramatically with increasing pH. Therefore, ozone can react directly to oxidize substrates or it can decay and generate free radicals in the process (U.S. EPA, 1999).

The existence of free radicals is the central feature of advanced oxidation processes (AOPs), which are addressed in section § 2.2.6.

One of main disadvantages of ozonation is due to the fact that ozone is an unstable molecule; therefore it must be generated on site and it is usually coupled with addition of a secondary disinfectant such as chlorine and chloramines. Online production of ozone is typically accomplished using an ozone generator fed with either dried air or oxygen. In such generators, ozone is formed by electrical discharge (10 to 30 kV range) in an air gap between two electrodes separated by a dielectric (e.g., between glass tubes). Efficient transfer of the ozone into solution is critical and is normally achieved by diffusion of the ozone-laden gas into a counter-current flow of water via bubble diffuser contactors, injectors or turbine mixers (U.S. EPA, 1999).

Other disadvantages of ozonation are: high capital as well operational and maintenance costs for ozonation equipment, high level of maintenance, operator skill, tendency to promote re-growth due to generation of BDOC/AOC, unless biologically active filtration (BAF) is used. Finally, ozone can produce a large variety of by-products, some of which may be much more toxic than their parent compounds (e.g. NDMA,  $\text{BrO}_3^-$ ).

### **2.2.5 Ultraviolet light irradiation**

UV radiation inactivates organisms by absorption of the light which causes a photochemical damage to RNA and DNA within microorganisms (thus preventing reproduction). UV radiation is very effective against bacteria and recently it has been shown to be effective also in viruses and protozoan cysts inactivation (Clancy et al., 2000).

UV electromagnetic energy is typically generated by the flow of electrons from an electrical source through ionized mercury vapour in a lamp. UV radiation occurs as electromagnetic waves with wavelengths between 100 and 400 nm, and therefore fits in the range between x-rays and visible light. UV radiation is sub-classified into smaller wavelength ranges as

UV-A (315-400 nm), UV-B (280-315 nm), UV-C (200-280 nm), and vacuum UV (100-200 nm). The germicidal UV light wavelengths range from 200 to 300 nm, with the optimum germicidal effect occurring at 253.7 nm, i.e., primarily in the UV-C range (U.S. EPA, 1999).

Several manufacturers have developed systems to align UV lamps in vessels or channels to provide UV light in the germicidal range for inactivation of microorganisms. UV-emitting lamps used for disinfection are classified as either low pressure or medium pressure. Conventional low-pressure UV lamps are the most energy efficient source, with approximately 40% of the electrical input power converted into UV-C light output at wavelength 254 nm, which is close to the wavelength of the maximum germicidal effect. Medium-pressure lamps are less electrically efficient than low-pressure lamps, but they produce much greater UV-C light intensity and thus achieve a given UV light dosage in a much shorter irradiation time. Irradiation wavelengths are spread throughout the UV (200-400 nm) and up into visible and near infrared ranges. In addition, not all wavelengths are equally effective at inactivating a target organism.

In water treatment, lamps are typically surrounded by quartz sheaths and are immersed in the flowing stream (closed or open vessel) (U.S. EPA, 1999).

The contact time required for UV disinfection is typically less than one minute. The effectiveness of disinfection by means UV radiation is affected by several water quality parameters, such as turbidity, suspended solids, colour, as well as, UV dose and flow-rate. Control of lamp fouling, due to water quality characteristics need to be considered. Since UV radiation instantaneously dissipates in water, a secondary disinfectant (such as chlorine or chloramine) is required in drinking water applications to maintain a residual throughout the distribution system.

### **2.2.6 Advanced oxidation processes (AOPs)**

Advanced oxidation processes (AOPs) generate highly reactive hydroxyl free radicals ( $\bullet\text{OH}$ ) to oxidize various compounds in the water. Since the mid-1970s, AOPs have been investigated in order to oxidize compounds that are resistant to conventional redox processes.

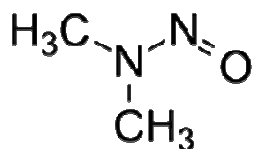
For the processes to be effective, the hydroxyl radicals must be generated continuously “in situ” through chemical or photochemical reactions.

Since the first work with  $O_3/UV$ , several different AOPs have been studied. The most common process used to generate  $\bullet OH$  is through the use of combined catalytic oxidants such as ozone-ultraviolet ( $O_3/UV$ ), hydrogen peroxide-ultraviolet ( $H_2O_2/UV$ ) and hydrogen peroxide-ozone ( $H_2O_2/O_3$ ). Although all 3 of the above processes can produce  $\bullet OH$ , the  $O_3/UV$  process provides the maximum yield of  $\bullet OH$  per oxidant (Golfonopoulos and Nikolaou, 2007).

### 2.3 N-NITROSODIMETHYLAMINE (NDMA)

N-Nitrosodimethylamine (NDMA) is a small, polar molecule that is highly water soluble. It belongs with nitrosamines group, which are emerging disinfection by-products of health and regulatory concern (CDPH, 2009b). Historically, concerns about human exposure to NDMA had been mainly related to its occurrence in food, consumer products, and industrial sites because it had been used for several decades in a number of industrial applications and had been produced as a by-product during manufacturing of consumer products and cured food. However, NDMA has recently been identified as an emerging DBP since its occurrence in drinking water supplies in California and Canada was shown to be related to chlorine-based disinfection processes (OMOE, 2004; Choi and Valentine, 2002a, 2002b; Mitch and Sedlak, 2002a, 2002b; Barrett et al., 2003; CDHS, 2006).

NDMA is organic nitrogen compound and its chemical structure is shown in Figure 2.2, whereas its physical and chemical properties are reported in Table 2.1.



**Figure 2.2** N-nitrosodimethylamine (NDMA) structure

**Table 2.1 Physical and chemical properties of N-nitrosodimethylamine (adapted from Merck, 1983 and HSDB, 1993)**

Molecular weight:	74.08
Boiling point:	151-153 °C
Melting point:	-41 °C
Density/specific gravity:	1.00048 at 20 °C
Vapor density:	2.56 (air = 1)
Vapor pressure:	2.7 mm Hg at 20 °C
Viscosity:	Low
Henry's law constant (37 °C):	$1.99 \times 10^{-6} \text{ atm} \cdot \text{m}^3/\text{mol}$
Log octanol/water partition coefficient ( $K_{OW}$ ):	-0.57

*Solubility: soluble in all common organic solvents and in lipids; very soluble in water, alcohol, and ether; miscible with dichloromethane and vegetable oils*

In this section several information concerning with the toxicity and carcinogenicity, occurrence and regulation of NDMA are reported. Formation mechanisms during different disinfection and oxidation processes are illustrated along with an overview of potential NDMA precursors and technologies used to control NDMA or its precursors concentrations.

### 2.3.1 NDMA health concerns and exposure

Since the first discovery was made in 1956 that rats fed with NDMA developed a high occurrence of hepatic tumours (Magee and Barnes, 1956), a significant amount of research has been conducted regarding the carcinogenic behaviour of nitrosamines including NDMA. NDMA is reasonably anticipated to be a human carcinogen based on sufficient evidence of carcinogenicity in experimental animals (IARC, 1978). Oral administration, inhalation, or intramuscular injection of NDMA into mice and rats induced tumours in their livers, lungs, and kidneys. Although no adequate studies have been reported regarding the relationship between exposure of NDMA and human cancer, NDMA is considered a potent human carcinogen due to similarities of metabolism to reactive intermediates between humans and animals (IARC, 1978; ATSDR, 1989; Linjinsky, 1983). The US EPA also classifies NDMA as a “prob-

able human carcinogen” and has set its  $10^{-6}$  cancer risk level in drinking water at 0.7 ng/L (USEPA, 1993). Besides occupational exposure to NDMA related to industrial uses, the general population may be exposed to unknown quantities of NDMA through ingestion, inhalation, and dermal contact. NDMA is widespread in a variety of foods including cheeses, soybean oil, meat products, and canned fruit (Sen et al., 1980; Fine et al., 1977), beverages (Scanlan et al., 1980), and tobacco smoke (Spencer and Westcott, 1976), as well as even in the air in certain industrial areas, notably in the rubber and leather tanning industries (Fajen et al., 1979; Brewer et al., 1980). NDMA was also reported to be possibly formed from nitrite or nitrate in the stomach or gastrointestinal tract (Mirvish, 1975; Bartsch and Montesano, 1984; Pignatelli et al., 1993). Potential human exposure to NDMA is expected, at levels of a few micrograms per day, from air, diet, and smoking, and its concentrations in aforementioned foods have been ranged between 0 and 85  $\mu\text{g}/\text{kg}$  (DHHS, 2005). Although NDMA can be formed in a variety of places, it does not persist in air or water in the open environment because it is rapidly decomposed by sunlight (HEEP, 1980).

### **2.3.2 Occurrence and regulation**

Most studies have found that NDMA formation is more associated with chloramination than with chlorination (Boyd et al., 2011; Mitch et al., 2009; Russell et al., 2012) (Table 2.2). Systems with high plant effluent NDMA ( $>50$  ng/L) typically used chloramines as the primary rather than secondary disinfectant (Russell et al., 2012). Due to the long time-scales of nitrosamine formation, plants with long in-plant chloramine contact times (e.g., 12-18 h) tended to have higher NDMA in the plant effluent than those with short (e.g., 0.5-2 h) contact times (Krasner et al., 2012a), and NDMA concentrations tend to increase throughout chloraminated distribution systems (Krasner et al., 2009a, 2012b, 2012c; Liang et al., 2009; Valentine et al., 2005).

In the largest study in the U.S.A., the USEPA UCMR2 ( $\sim 1200$  systems) (USEPA, 2012), NDMA was detected ( $>2$  ng/L) in 34% of chloramine plant effluents, but only 3% of chlorination plant effluents (Russell et al., 2012). When detected in chlorinated plant effluents, NDMA may have been derived from the source waters (Boyd et al., 2011).



**Table 2.2 NDMA occurrence in various nationwide in North America (Krasner et al., 2013)**

Survey	Reference	Disinfectant	Sample location	NDMA (ng/L)				
				Minimum	Median	75 <sup>th</sup> percent.	90 <sup>th</sup> percent.	Maximum
U.S. and Canada	Krasner (2009)	Chlorine	Plant eff.	ND	ND	ND	1.0	2.4
			Dist. Syst.	ND	ND	1.1	1.2	1.9
		Chloramines	Plant eff.	ND	ND	1.4	3.3	6.6
			Dist. Syst.	ND	1.7	2.8	4.9	22
		Chlorine	Plant eff.	20	25	26	-	30
			Dist. Syst.	10	12	-	-	24
U.S. and Canada	Boyd et al. (2011)	Chlorine	Source	ND	2.1	4.2	-	9.4
			Plant eff.	ND	4.0	5.3	-	17
			Dist. Syst.	ND	ND	9.0	-	20
		Ozone/ chlorine	Source	ND	ND	ND	-	4.7
			Plant eff.	ND	ND	2.5	-	3.5
			Dist. Syst.	ND	ND	6.3	-	12

**Table 2.2 (continue)**

Survey	Reference	Prim./sec. disinfectant	Sample location	NDMA (ng/L)				
				Minimum	Median	75 <sup>th</sup> percent.	90 <sup>th</sup> percent.	Maximum
U.S. and Canada	Boyd et al. (2011)	Chloramines	Source	ND	ND	ND	ND	4.7
			Plant eff.	ND	7.5	14	24	29
			Dist. Syst.	ND	4.9	10	-	130
U.S.	Mitch et al. (2009)	Chlorine	Plant eff.	ND	ND	ND	ND	ND
		Chloramines	Plant eff.	ND	ND	3.3	10	20
U.S.	Krasner et al. (2012)	Chloramines	Source	ND	ND	ND	ND	ND
			Plant eff.	ND	5	8	-	17
			Dist. Syst.	1.8	12	14	-	16
U.S.	Russell et al. (2012) <sup>b</sup>	Chlorine	Plant eff.	ND	ND	ND	ND	62
			Dist. Syst.	ND	ND	ND	ND	85
		Chloramines	Plant eff.	ND	ND	ND	4.9	470
			Dist. Syst.	ND	ND	3.8	8.2	630

<sup>a</sup> Groundwater with anion exchange resin. <sup>b</sup> Based on UCMR2. Assumes non-detects are equal to zero

Alternatively, NDMA formed as a result of chlorination may be attributable to high source water ammonia concentrations (e.g., 0.7-1.9 mg N/L (Tugulea et al., 2008)), as chlorination of ammonia-containing waters can lead to effective chloramination. This occurs if the chlorine dose is insufficient to lead to breakpoint chlorination, which requires 7.6 mg/L of  $\text{Cl}_2$  per mg/L as N of ammonia (White, 1999). NDMA was the most commonly detected specific nitrosamine. On the rare occasions when other nitrosamines were detected, NDMA concentrations tended to be higher (Krasner, 2013).

Nitrosamine occurrence surveys have been performed in the United Kingdom, as chloramination was uncommon in other parts of Europe. In England and Wales, only three of 41 surveyed plants had detectable NDMA, and the concentrations were always below 6 ng/L (Dillon et al., 2008).

In another study in the UK (Templeton and Chen, 2010), NDMA was barely above the method detection limit (0.9 ng/L) in a few isolated samples in one distribution system. In Scotland, NDMA was only found at one works, which used chloramines, of seven surveyed (Goslan et al., 2009). Low NDMA occurrence in the UK was not surprising, as chloramine plants in the UK typically operated with a set (e.g., 30 min) pre-chlorine contact time and low (i.e., 0.5 mg/L as  $\text{Cl}_2$ ) chloramine concentrations (Templeton and Chen, 2010). Nitrosamine occurrence in Australia was relatively high, due to the high prevalence of chloramination, wastewater recycling, and effective chloramination resulting from high source water ammonia concentrations. One study (Newcombe et al., 2012) detected NDMA in 75% of chloraminated waters and 37% of these detections had NDMA concentrations >10 ng/L. NDMA was detected in 88% of chlorinated recycled wastewaters, and 33% of chlorinated drinking waters. In Western Australia, relatively high incidences of NDMA in chlorinated water (33%) were observed, possibly due to high source water ammonia concentrations (Liew et al., 2011). In recent surveys of Chinese waters, nitrosamines occurred frequently, often due to contamination from industrial and domestic wastewaters (Wang et al., 2011a, 2011b). Compared to other countries, nitrosamines other than NDMA have been more frequently detected in China. A study on Chinese source waters found detectable levels of seven nitrosamines, including NDMA, in surface waters, with concentrations >5 ng/L on average (Ma et al., 2012). In Japan, NDMA was detected in raw waters at up to 4.3 ng/L, but NDMA concentrations were generally lower in finished

drinking water, because chlorination was almost exclusively used in Japan (Asami et al., 2009). However, NDMA was detected at 10 ng/L in the effluent of an ozone plant, as the source water contained anti-yellowing agents, which were found to be a NDMA precursor during ozonation (Kosaka et al., 2009). NDMA was detected in distribution systems in Singapore, but was shown to occur at relatively low concentrations (1.1-6.4 ng/L) (Zhang et al., 2010).

Wastewater were reported often to contain significant concentrations of NDMA and other nitrosamines (Sedlak et al., 2005; Krauss et al., 2009) as well as considerable concentration of NDMA precursors (Krasner et al., 2009). In the U.S.A., Sedlak et al. (2005) found NDMA in concentrations ranging from 80 to 790 ng/L in seven wastewater treatment plant influents. Astonishingly, in California two drinking water production wells, under the influence of recharge water from the RO wastewater treatment system of the Orange County Water District's Water Factory 21, were shut down due to the detection of 30 to 40 ng/L of NDMA (OCWD, 2000).

Due to NDMA toxicity and carcinogenicity, USEPA included NDMA in the monitoring program "Unregulated Contaminant Monitoring Rule 2" (UCMR2) (USEPA, 2012) and on the drinking water contaminant candidate list 3 (CCL3) (USEPA, 2009), i.e. a list of contaminants that are currently not subject to any proposed or promulgated national primary drinking water regulations, that are known or anticipated to occur in public water systems, and which may require regulation.

To date only few regulatory agencies have already established standards for NDMA in drinking water. CDPH (2009b) set 10 ng/L notification levels for NDMA in drinking water and California's Office of Environmental Health Hazard Assessment (COEHHA) set 3 ng/L as public health goal (COEHHA, 2006). Always in the USA, Massachusetts has a guideline value of 10 ng/L (MDEP, 2004). Canada has set a 40 ng/L national guideline value (Health Canada, 2011), whereas the Ontario Ministry of the Environment has a maximum allowable concentration for NDMA of 9 ng/L in drinking water (Government of Ontario, 2002).

The World Health Organization (WHO) set a guideline value of 100 ng/L which was adopted as target value by Japan (WHO, 2008; Van Huy et al., 2011) and Australia (Australia, 2011).

### 2.3.3 NDMA formation during chloramination

Chloramination is responsible for nitrosamine formation. Early mechanistic research suggested nitrosamine formation by a reaction between monochloramine ( $\text{NH}_2\text{Cl}$ ) and organic amine precursors (Choi and Valentine, 2002a; Mitch and Sedlak, 2002b). The formation of NDMA in this environment is consistent with a reaction involving the slow formation of unsymmetrical dimethylhydrazine (UDMH) via a nucleophilic substitution reaction between uncharged DMA and  $\text{NH}_2\text{Cl}$ , followed by the rapid oxidation of UDMH to a variety of products, including NDMA. Subsequent mechanistic research indicated that monochloramine was not a significant precursor; nearly all nitrosamine formation could be explained via reactions involving the low concentrations of dichloramine ( $\text{NHCl}_2$ ) (i.e., ~5%) that always coexist with monochloramine under typical chloramination conditions according to the equilibrium (Schreiber and Mitch, 2006a):



Briefly, the nucleophilic attack of unprotonated secondary amines on dichloramine forms a chlorinated unsymmetrical dialkylhydrazine intermediate (e.g., Cl-UDMH), which is then oxidized by dissolved oxygen to the corresponding nitrosamine. Figure 2.3 shows the NDMA formation mechanisms by chloramination.

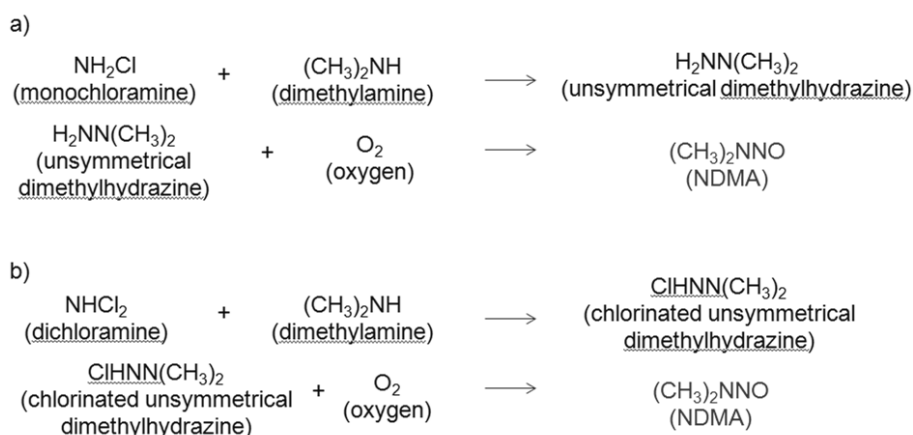


Figure 2.3 NDMA formation scheme; a) formation by monochloramine; b) formation by dichloramine

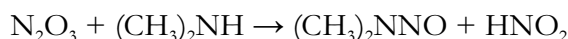
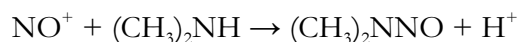
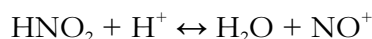
The reaction occurs slowly (i.e., days), indicating that nitrosamines should accumulate within chloraminated distribution systems (Mitch et al., 2003a, 2003b). Additional studies with model precursors, described later, demonstrated that tertiary and quaternary amines also serve as nitrosamine precursors. Molar yields of NDMA from most model secondary and tertiary amines were ~2% (Mitch and Sedlak, 2004), and were an order of magnitude lower for quaternary amines (Kemper et al., 2010). However, yields from chloramination of tertiary amines containing a  $\beta$ -aromatic ring (e.g., ranitidine) were up to ~90% (Shen and Andrews, 2011a). Formation increased with pH due to the increasing prevalence of the active unprotonated form of the amines. Application of chloramines to authentic source waters indicated that NDMA formation increases with temperature (Krasner et al., 2012b). Because this pathway relates to the predominant association of nitrosamine formation with chloramine disinfection, this reaction pathway is likely the most important pathway for drinking water treatment. Recent mechanistic research suggests that bromide catalyzes the formation of NDMA during chloramination, even though it seems that bromide promotion generally is only important for high-bromide waters (Le Roux et al., 2012; Luh and Marinas, 2012).

Nitrosamine formation may also increase up to four-fold during breakpoint chlorination (Schreiber and Mitch, 2007). The reaction is rapid (<1 h), and appears to derive from the formation of reactive nitrogen species formed during chloramine decay at the breakpoint. However, this enhancement was observed at a limited range of chlorine to ammonia molar ratios near 1.7:1 (8.6:1 weight ratio), where negligible residual chlorine was measured. With a sufficient chlorine dosage to maintain a free chlorine residual (e.g., 2:1 molar ratio), the enhancement in NDMA formation was not significant. In a range of authentic waters, NDMA formation was found to be significant in the region approaching breakpoint in highly wastewater-impacted drinking waters (Krasner et al., 2012b).

#### **2.3.4 NDMA formation by nitrosation**

Since nitrosamines were identified as powerful carcinogens, nitrosation of secondary amines has been thoroughly investigated, with special emphasis on in vivo formation of nitrosamines such as in foods, human stomachs, and water supplies (Williams, 1988). N-nitrosation is the reaction of amines (mostly secondary amines and to a lesser extent tertiary

amines) with a nitrosating agent such as nitrous acid which readily decomposes to a nitrosyl cation or forms dinitrogen trioxide in the acidic conditions. However, much stronger acidic conditions are needed to obtain the nitrosyl cation from nitrous acid compared to formation of dinitrogen trioxide. The nitrosyl cation or dinitrogen trioxide then reacts with amines such as dimethylamine (DMA) to form NDMA as shown in the following equations:



Since the reaction of an amine with  $\text{N}_2\text{O}_3$  is usually faster than hydrolysis of  $\text{N}_2\text{O}_3$  to nitrous acid, the rate-limiting step becomes the formation of  $\text{N}_2\text{O}_3$  that is favored in the presence of acid (Challis and Kyrtopoulos, 1977).

This N-nitrosation is believed to be responsible for NDMA occurrence in many foods such as malt grains, fish, dried or canned foods, and, especially, meat products cured with nitrite (Mitch et al., 2003b).

However, NDMA formation in water treatment facilities where circumneutral pH and low nitrite concentration are mostly encountered is not well explained by the classical N-nitrosation mechanism since the nitrosyl cation or  $\text{N}_2\text{O}_3$  formation in N-nitrosation requires strong acidic conditions. The most rapid N-nitrosation reaction was reported at pH 3.4 where an optimum condition between the demand for protonation of nitrite ( $\text{pK}_a$  of nitrite = 3.35) and the need of unprotonated dimethylamine exists ( $\text{pK}_a$  of DMA = 10.7) (Mirvish, 1975). Some studies have reported that N-nitrosation can be catalyzed at circumneutral pH by photochemical reactions (Ohta et al., 1982; Lee and Yoon, 2007a) or by formaldehyde (Keefer and Roller, 1973) and fulvic acid (Weerasooriya and Dissanayake, 1989). More Recently, Choi and Valentine (2003) reported that the formation of NDMA from the reaction of DMA and nitrite can be greatly enhanced by the presence of free chlorine at pH 7. The authors attributed the enhancement of N-nitrosation even at neutral pH to the formation of a highly reactive nitrosating intermediate such as

dinitrogen tetroxide ( $\text{N}_2\text{O}_4$ ) during the oxidation of nitrite to nitrate by free chlorine. The reaction is rapid (i.e.,  $<1$  h), but the yields are approximately two orders of magnitude lower than for the chloramination pathway. There are also some theoretical papers predicting catalytic nitrosation of DMA in the presence of carbon dioxide and carbonyl compounds (Lv et al., 2007; Lv et al., 2009).

### 2.3.5 NDMA formation during ozonation

While ozonation of typical secondary amine precursors may form NDMA, yields are low (i.e., 0.02%) (Andrzejewski et al., 2008; Yang et al., 2009) unless additional inorganic constituents as hydroxylamine (HA) were present (yields of  $\sim 0.45\%$  were observed) (Padhye et al., 2011; Andrzejewski et al., 2012). However, for a limited subset of precursors containing hydrazine (e.g., unsymmetrical dimethylhydrazine and semicarbazides) or sulfamide (e.g., N,Ndimethylsulfamide functionalities) functional groups, yields could be  $>50\%$  (Kosaka et al., 2009; Schmidt and Brauch, 2008; Shen and Andrews, 2011b; Von Gunten et al., 2010). The reactions are rapid (i.e.,  $<1$  h) and, in the case of sulfamides, bromide catalysis was significant at concentrations as low as 15 mg/L (Von Gunten et al., 2010).

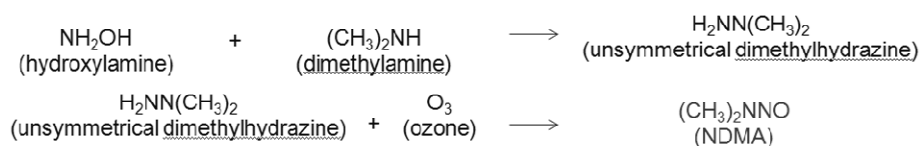
Yang et al. (2009) reported two alternative pathways that possibly explain NDMA formation during ozonation of secondary amines at neutral and alkaline pH: (i) DMA precursor reacting with HA to form UDMH, that is further oxidized to NDMA and (ii) a nitrosation pathway in which dinitrogen tetroxide ( $\text{N}_2\text{O}_4$ ) acts as the nitrosating reagent.

During the hydroxylamine pathway, secondary amines are easily oxidized by ozone to HA, although yields are poor due to overoxidation (Streitwieser and Heathcock, 1981; von Gunten, 2003). Then the reactive intermediate UDMH is formed via a nucleophilic substitution reaction between HA and the remaining DMA. In addition, Padhye et al. (2011) showed that the presence of ozone is critical during reaction of HA with DMA to yield NDMA and that UDMH formed 3 orders of magnitude more NDMA when oxidized by ozone than by oxygen. NDMA formation by hydroxylamine pathway is shown in Figure 2.4.

About the nitrosation pathway, it is well-known that hydroxyl radicals are formed due to the decomposition of ozone (Stachelin and Hoigne, 1982), and more DMA could be degraded into nitrite or other nitrogenous products under these conditions. Nitrite can be oxidized rapidly by



hydroxyl radicals and forms  $N_2O_4$ .  $N_2O_4$  exists in two isomeric forms,  $ON-ONO_2$  and  $O_2N-NO_2$ , which are very effective nitrosating and nitrating agents, respectively. The nitrosation of DMA by asymmetrical  $N_2O_4$  ( $ON-ONO_2$ ) was proven to contribute to NDMA formation (Lv et al., 2008).



**Figure 2.4 NDMA formation scheme during hydroxylamine pathway**

Yang et al. (2009) supposed that the nitrosation should be the major pathway for NDMA formation during ozonation under acid condition and the maximum yield occurs around pH 3. However, this pathway cannot explain the observed increased yield on NDMA with increasing pH at neutral and alkaline conditions, since such reaction would have lower NDMA yield at higher pH (Keefer and Roller, 1973). The hydroxylamine pathway can be used to explain the NDMA formation under neutral and alkaline conditions where the nitrosation contribution is minimal (Yang et al., 2009; Padhye et al., 2011). In fact, the formation of UDMH is a well-known alkaline catalytic reaction (Mitch and Sedlak, 2002a).

### 2.3.6 NDMA precursors

Chloramination is the major cause of nitrosamine formation in North American drinking waters, and amines are expected to be the major source of precursors during chloramination. Amides, the other major category of organic nitrogen precursors, react orders of magnitude more slowly than amines with chloramines, due to the electron withdrawing carbonyl groups adjacent to the nitrogen (Mitch and Sedlak, 2004; Walse and Mitch, 2008). Although nitrosamine formation from amides is low over short chloramines contact times, the slow release of secondary amines from certain amides by hydrolysis can form significant concentrations of nitrosamines over timescales of  $\sim 1$  week (Mitch and Sedlak, 2004). Examples include the solvent dimethylformamide and the herbi-

cides dimethyldithiocarbamate and diuron (Chen and Young, 2008; Mitch and Sedlak, 2004; Padhye et al., 2013).

Although primary amines can be nitrosated, primary nitrosamines decay nearly instantaneously, releasing nitrogen gas and a carbocation. Thus primary nitrosamines have not been isolated (Ridd, 1961). Most mechanistic research has addressed secondary amines (Choi and Valentine, 2002a; Mitch and Sedlak, 2002b; Schreiber and Mitch, 2006a; Shah and Mitch, 2012), which can directly form stable secondary nitrosamines. While most research has focused on NDMA formation from dimethylamine (DMA), other secondary amines can form their corresponding nitrosamines upon chloramination (Schreiber and Mitch, 2006b).

Tertiary amines may also serve as significant precursors. Upon exposure to chlorine, tertiary amines decay nearly instantaneously and quantitatively to release an aldehyde and a secondary amine capable of forming a stable secondary nitrosamine upon subsequent chloramination (Mitch and Schreiber, 2008). There was no regioselectivity regarding which of the alkyl substituents on the tertiary amines were eliminated as the aldehyde. Similar reactions pertain to chloramination of tertiary amines, although the conversion of the tertiary amine to a secondary amine was slower due to the lower reactivity of chloramines compared to chlorine. The net result is that nitrosamine yields from most tertiary amines during chloramination are comparable to those from secondary amines (i.e., ~2%).

However, a subset of tertiary amines, where one of the alkyl substituents contained an aromatic group in the  $\beta$ -position to the nitrogen (e.g., a benzyl functional group), exhibit far higher yields of NDMA during chloramination (Le Roux et al., 2011; Shen and Andrews, 2011a, 2011b). Such functional groups are observed in certain pharmaceuticals. For example, ranitidine, the active component in the antacid Zantac, formed NDMA at yields of 60-90% (Le Roux et al., 2011; Shen and Andrews, 2011a, 2011b). These higher yields suggest that these tertiary amines can form nitrosamines without proceeding through a secondary amine intermediate, although the specific pathway is unclear.

Although the positive charge on quaternary amines hinders reactions with chloramines, model quaternary amines formed NDMA at yields ~0.2%, likely via pathways involving degradation of quaternary amines to secondary amines initiated by radicals (Kemper et al., 2010; Padhye et al., 2010). As indicated below, quaternary amines are important functional groups in personal care products (e.g., shampoos), and materials

used for drinking water treatment (e.g., cationic coagulation polymers and certain anion exchange resins).

NDMA formation from organic matter isolates in the presence of monochloramine requires one nitrogen atom in organic matter to react with inorganic nitrogen in chloramines, based upon  $^{15}\text{N}$ - $\text{NH}_2\text{Cl}$  experiments (Mitch et al., 2009). Generally, the hydrophilic fractions tended to form more NDMA than hydrophobic fractions, and base fractions tend to form more NDMA than acidic fractions when normalized to a carbon basis (Chen and Valentine, 2007). NDMA yields (ng NDMA/mg DOC) ranged from 22 to 78 in one study (Chen and Valentine, 2007), but after accounting for the contribution of each fraction to the total DOC of the river water, the low reactivity of the hydrophobic acid fraction still accounted for nearly 70% of the NDMA formation potential (NDMA FP). Recent field and bench-scale studies show that certain rubber seals and gaskets in potable water systems can be a source of NDMA in chloraminated water systems (Morran et al., 2011; Teefy et al., 2011). While PVC pipe materials were relatively unreactive in forming NDMA in chlorinated or chloraminated water, rubber components (pipe rubber ring joint lubricant [in the form of water-soluble gel]; natural rubber seal rings, ethylene propylene diene terpolymers and styrene-butadiene rubber) leached NDMA in chlorine-free water and formed NDMA after chloramination (Morran et al., 2011).

Whereas nitrosamine formation during chloramination has been largely investigated, there is a knowledge lack about nitrosamine formation upon ozonation and particularly about the precursor pool. DMA (Andrzejewski et al., 2008), tolylfuanid, its decomposition by-products (e.g. dimethylsulfamide (DMS)), daminozide, and its decomposition by-products 1,1-dimethylhydrazine (UDMH) (Schmidt and Brauch, 2008) have been shown to be precursors of NDMA upon ozonation. In addition, some dyes and related compounds were shown to produce NDMA during ozonation (Oya et al., 2008). The molar conversion yields of tolylfuanid, daminozide, and their decomposition products to NDMA by ozonation range from 9 to 80% (Schmidt and Brauch, 2008). On the other hand, the molar conversion yields of DMA and these reported dyes and related compounds (e.g., methylene blue and N,N-dimethyl-p-phenylenediamine) to NDMA were on order of 0.01%, and therefore, their contributions to NDMA precursors in environmental water were considered to be very low. Noteworthy is that NDMA production from DMA increased when the inorganic constituent HA was spiked during

ozonation (Padhye et al., 2011; Andrzejewski et al., 2012). In addition, Padhye et al. (2011) observed NDMA formation from ozonation of several water treatment polymers, including polyamines and cationic polyacrylamides. Particularly, poly(diallyldimethylammonium chloride) (polyDADMAC) yielded the highest amount of NDMA among the studied polymers and the NDMA formation was related to the DMA release. In general NDMA presence and formation are generally low in pristine water bodies (Gerecke and Sedlak, 2003), while wastewater often contains significant concentrations of NDMA and other nitrosamines (Sedlak et al., 2005; Krauss et al., 2009) as well as considerable concentrations of NDMA precursors (Krasner et al., 2009).

### 2.3.7 NDMA removal

Because they are fairly hydrophilic (e.g.,  $K_{OW} = 0.27$  for NDMA) (ATSDR, 1989; Mitch et al., 2003b), nitrosamines sorb poorly to activated carbon. Furthermore, chloramines are typically added after activated carbon treatment, so nitrosamines will normally not be present in drinking waters treated by activated carbon. Because adsorption of nitrosamines after formation is not feasible, sorption can only be applied for the removal of nitrosamine precursors.

Ultraviolet (UV) irradiation has been known to be an efficient method for removing NDMA. Based on the strong UV absorption of NDMA at 227 nm and 332 nm with the quantum yield of 0.13 for NDMA photolysis in aqueous solution (Sharpless and Linden, 2003), several studies have reported that NDMA-contaminated water can be effectively treated by UV using low pressure or medium pressure Hg lamps (Jobb et al., 1994; Sharpless and Linden, 2003; Stefan and Bolton, 2002). In addition, NDMA photolysis seems to be favored by acid conditions (Stefan and Bolton, 2002). Because a UV fluence of  $\sim 1000$  mJ/cm<sup>2</sup> is required for a log order reduction in NDMA (Sharpless and Linden, 2003), UV treatment for nitrosamine destruction is more expensive than for disinfection. While effective for destruction of nitrosamines, UV treatment at fluence near 1000 mJ/cm<sup>2</sup> is only partially effective at destruction of nitrosamine precursors (Krasner et al., 2013).

During spiking experiments with surface water, ozone alone had little impact on the removal of NDMA (12% removal at 10 mg O<sub>3</sub>/L) but ozone with peroxide achieved a similar level of destruction with significantly less ozone (12% removal at 1.5 mg O<sub>3</sub>/L + 0.5 mg peroxide/L).

and 46% removal at 10 mg O<sub>3</sub>/L + 3.5 mg peroxide/L) (Pisarenko et al., 2012). In both cases the NDMA destruction was limited and the levels of degradation were consistent with the second-order ozone ( $k_{O_3} = 5.3 \times 10^{-2} \text{ M}^{-1} \text{ s}^{-1}$ ) and  $\cdot\text{OH}$  ( $k_{\cdot\text{OH}} = 4.6 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ ) rate constants for NDMA (Lee et al., 2007b). In wastewater net direct formation of NDMA was observed after either ozone or ozone/peroxide treatment (Pisarenko et al., 2012).

### 2.3.8 NDMA precursors removal

Because nitrosamines can continue to form in distribution systems unless the precursors have been removed or transformed, several studies have been focused on NDMA precursors removal by different water and wastewater treatments. Activated sludge treatments were shown to be able to remove small polar and charged NDMA and other nitrosamines' precursors to about 80%. In contrast, less polar precursors resulted more recalcitrant (Krauss et al., 2010). In a study conducted in 12 wastewater treatment plants (WWTP) in Japan (Yoon et al., 2011), the rate of NDMA formation potential (NDMA FP) reduction from influent to secondary effluent varied between 85% and 98%. NDMA FP was also reduced in surface water and municipal wastewater effluent by powdered activated carbon (PAC) and granular activated carbon (GAC) (Sacher et al., 2008, Hanigan et al., 2012). In both the treatments, removal of NDMA FP exceeded removal of DOC and UV, surrogate measures for traditional disinfection by-products (DBP) (Hanigan et al., 2012). RO resulted as a very effective treatment on NDMA precursors removal. Apart from larger molecules, RO affects also small charged precursors such as dimethylamine (DMA), and only small uncharged molecules such as dimethylsufamide or dimethylformamide (DMF) can probably pass RO membranes to a larger extent (Mitch and Sedlak, 2004; Krauss et al., 2010). On the other hand, reverse osmosis doesn't appear to be very efficient in NDMA rejection; removal ranging from negligible up to 86% is reported in literature (Plumlee et al., 2008; Fujioka et al., 2012; Fujioka et al., 2013). However, the combination of RO with UV treatment enables the achievement of final concentration of NDMA in compliance with water reuse requirements (Ontario Ministry of the Environment, 2006; California Department of Public Health, 2010). Recently, several studies reported an enhanced NDMA formation in presence of chloramine after UV irradiation or UV/H<sub>2</sub>O<sub>2</sub> treatment of swimming pool water and se-

lected pharmaceuticals (Chen et al., 2011; Redjenovic et al., 2012; Farré et al., 2012; Soltermann et al., 2013). The effect of UV and UV/H<sub>2</sub>O<sub>2</sub> on NDMA precursors and their degradation is particularly relevant and it needs a deeper investigation, as these technologies are considered the best available to remove NDMA from water (USEPA, 2008), specially for water reuse application.

## 3 MATERIALS AND METHODS

### 3.1 MATERIALS AND WATERS USED

#### 3.1.1 West Basin wastewater reclamation plant (WWRP)

Part of experiments was conducted using water samples from West Basin wastewater reclamation plant (WWRP), a water treatment plant (WWRP) placed in El Segundo (Los Angeles), California (USA). The reclamation plant receives a wastewater secondary effluent from an upstream wastewater treatment plant (WWTP) (named Hyperion WWTP) that treats large part of sewages produced in the city of Los Angeles, California (USA). West Basin WWRP is able to produce through advanced technologies recycled water of qualities necessary for potable and non-potable applications. One line of treatment is utilized to recycle water for indirect potable application by injection in aquifer. This line of the plant has the capacity to produce 47318 m<sup>3</sup>/d of water which is used to protect the South bay's coastal groundwater reservoirs against saltwater intrusion from the Pacific Ocean. Later, this groundwater is pumped out from drinking water wells and treated for potable water supply. The process scheme of the IPR system includes microfiltration (MF), reverse osmosis (RO), advanced oxidation processes (i.e. UV/H<sub>2</sub>O<sub>2</sub>), decarbonation, lime stabilization (pH 8) and final disinfection by sodium hypochlorite (NaClO) (dose of 4 mg/L as chlorine (Cl<sub>2</sub>)) (Figure 3.1).

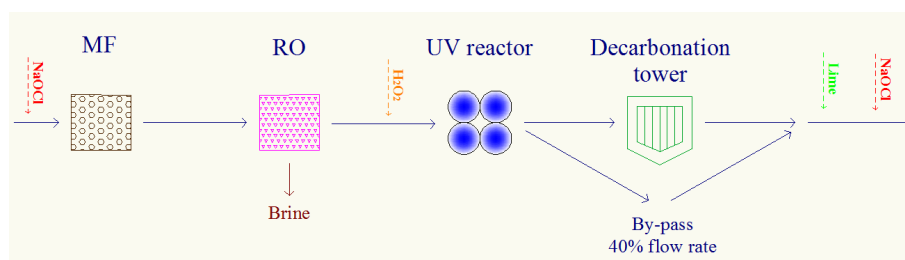


Figure 3.1 Scheme of West Basin WWRP. MF, Microfiltration; RO, reverse osmosis; NaOCl, sodium hypochlorite; H<sub>2</sub>O<sub>2</sub>, hydrogen peroxide

Decarbonation towers strip carbon dioxide ( $\text{CO}_2$ ) raising the pH and reducing the amount of lime to add for stabilizing the water and reaching pH 8. Based on pH control and saturated lime alkalinity, about 60% of the flow is sent to the decarbonation towers and the remaining 40% is bypassed.  $\text{NaClO}$  (10 mg/L as  $\text{Cl}_2$ ) is also added before MF for membranes fouling control; chloramines are formed because of the elevated ammonia load present in water (Table 3.1).

**Table 3.1 Water quality parameters at West Basin WWRP**

Water parameter	RO feed	RO permeate	Final effluent	Pilot system effluent
Chloride (mg/L)	158.0	4.1	8.2 (1.9) <sup>e</sup>	7.4
Nitrate (mg/L as N <sup>a</sup> )	2.0	0.4	0.6 (0.2)	0.4
Nitrite (mg/L as N)	0.5	0.1	0.2 (0.1)	n.a. <sup>f</sup>
Ammonia (mg/L as N)	39.0	2.1	2.9 (0.5)	3.0
TKN <sup>b</sup> (mg/L)	42.0	3.2	3.1 (0.3)	3.1
TN <sup>c</sup> (mg/L)	42.7	3.7	5.5 (1.0)	6.8
DOC <sup>d</sup> (mg/L)	11.1	0.2	0.2 (0.1)	0.5

<sup>a</sup> N, nitrogen. <sup>b</sup> TKN, total kjeldahl nitrogen. <sup>c</sup> TN, total nitrogen. <sup>d</sup> DOC, dissolved organic carbon. <sup>e</sup> ( $\pm$  one standard deviation of the measurement derived from the standard curve). <sup>f</sup> n.a., not available.

The ultraviolet disinfection and oxidation system consists of three parallel trains. Each train is comprised of two chambers connected in series. Each chamber comprises two reactor also connected in series, while each reactor houses 72 low pressure lamps. All the reactors operate equally so that individual reactor performance can be considered additive. Sampling points are present between the second and third reactor and after the last reactor. The UV system operates in a steady state condition; the control system can only varies two parameters, output power and flow. As the lamps age or if there is a drop in transmissivity, the control system will increase power to achieve the target dose. If the calculated dose value cannot be met at 100% power, then the control system will reduce flow. Each reactor achieves a UV dose of at least 115  $\text{mJ}/\text{cm}^2$ . Figure 3.2 shows the UV system schematic.

Recently a pilot system (Figure 3.3), including ozone, chlorine addition, MF and RO, has been installed at the WWRP to get the design parameters for a full scale ozone system to be built before MF and chloramination in order to improve the biofouling control process and reduce the



back wash frequency of the MF and RO membranes. The pilot system receives the influent to West Basin WWRP.

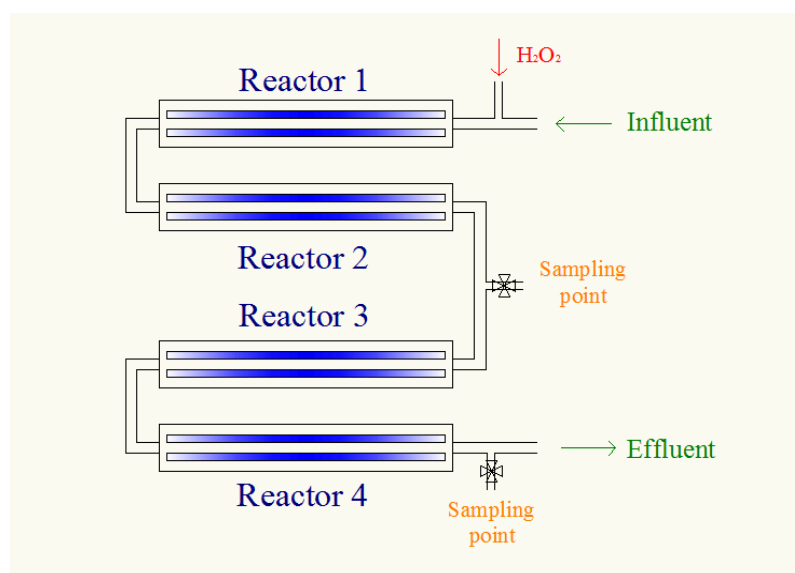


Figure 3.2 UV system at West Basin WWRP

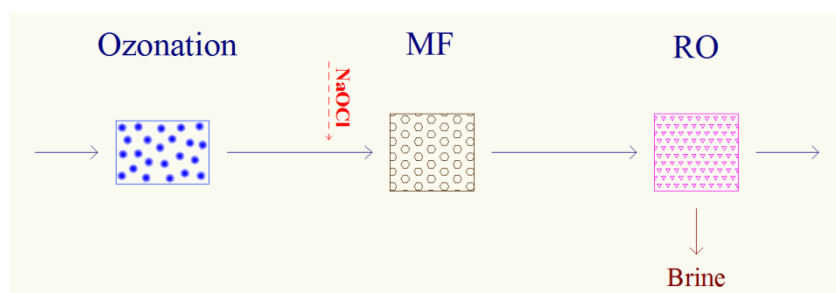


Figure 3.3 Pilot system at West Basin WWRP. MF, Microfiltration; RO, reverse osmosis; NaOCl, sodium hypochlorite

### 3.1.2 Hyperion wastewater treatment plant (WWTP)

Different campaigns of water samples collection were also conducted at Hyperion WWTP. The wastewater plant serves about four million people and treats wastewater characterized by about 90% from domestic discharges. Industrial sources are few and include textile factories and

carpet dye operations. The unchlorinated final effluent is in part discharged to the ocean and in part sent to the downstream WWRP (West Basin). Water quality parameters of plant influent, primary effluent and secondary effluent are shown in Table 3.2.

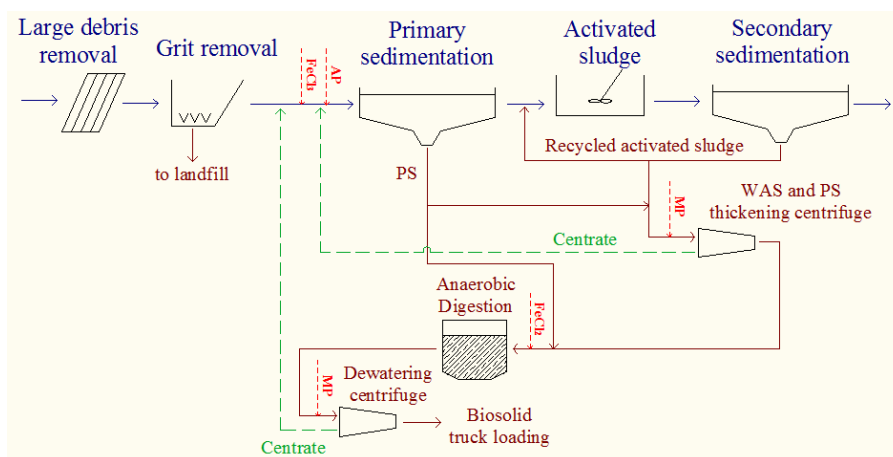
**Table 3.2 Typical water quality parameters at Hyperion WWTP**

Water parameter	Influent	Primary effluent	Secondary effluent
Conductivity ( $\mu\text{S}/\text{cm}$ )	1290	1150	1348 (104.7) <sup>i</sup>
Alkalinity (mg/L as $\text{CaCO}_3^a$ )	314	354	298 (24.8)
Sulfate (mg/L)	111	106	110 (5.6)
Chloride (mg/L)	154	194	199 (16.4)
Bromide ( $\mu\text{g}/\text{L}$ )	254	349	370
Nitrate (mg/L as $\text{N}^b$ )	0.3	0.2	4.0 (2.1)
Nitrite (mg/L as $\text{N}$ )	0.4	0.5	1.7 (0.7)
Ammonia (mg/L as $\text{N}$ )	38.8	50.5	40.6 (4.7)
TKN <sup>c</sup> (mg/L)	57	69	50 (0.5)
pH	7.6	7.7	7.7 (0.4)
SUVA <sup>d</sup> (L/mg m)	1.94	1.90	1.52 (0.1)
TOC <sup>e</sup> (mg/L)	n.a. <sup>l</sup>	66.7 (2.6)	14.7 (1.6)
DOC <sup>f</sup> (mg/L)	33.0	19.4	14.3 (1.9)
UV <sub>254</sub> <sup>g</sup> (1/cm)	0.639	0.368	0.210 (0.02)
TSS <sup>h</sup> (mg/L)	n.a.	2105 (259.9)	11.75 (2.7)

<sup>a</sup>  $\text{CaCO}_3$ , calcium carbonate. <sup>b</sup> N, nitrogen. <sup>c</sup> TKN, total kjeldahl nitrogen. <sup>d</sup> TN, total nitrogen. <sup>e</sup> SUVA, specific UV absorbance. <sup>f</sup> TOC, total organic carbon. <sup>g</sup> DOC, dissolved organic carbon. DOC was measured after 0.7  $\mu\text{m}$  filtration. <sup>h</sup> UV<sub>254</sub>, UV absorbance at 254 nm. <sup>i</sup> TSS, total suspended solids. <sup>j</sup> ( $\pm$  one standard deviation of the measurement derived from the standard curve). <sup>l</sup> n.a., not available. Reported TOC and TSS values of WWTP primary effluent are related to October 2012 monthly average.

The plant scheme consists of preliminary treatments, primary sedimentation and secondary treatment where high-purity-oxygen is directly bubbled into the activated sludge reactor having a sludge retention time of 1.5 days. Sludge from the secondary treatment is transferred to the waste activated sludge (WAS) thickening centrifuges. In addition, part of the sludge from primary treatment is also moved to these centrifuges. Primary sludge (PS) and thickened WAS are pumped together to the anaerobic digesters operating under thermophile condition at about 53°C with direct steam injection for stabilization and solids reduction and with a sludge retention time of about 15 days. Finally, the digested sludge is pumped to the dewatering centrifuges. Supernatant from dewatering centrifuges and WAS thickening (WAST) centrifuges are sent back to the

head of the plant. Dewatered biosolids are trucked offsite for use through a diversified management plan utilizing 100% beneficial use. The whole plant scheme is shown in Figure 3.4.



**Figure 3.4** Scheme of Hyperion WWTP. MP, Mannich polymer; AP, anionic polymer;  $\text{FeCl}_2$ , Ferrous chloride;  $\text{FeCl}_3$ , Ferric chloride; PS, primary sludge; WAS, waste activated sludge.

The cationic polymer Mannich is used as a chemical conditioning agent for WAS thickening centrifuges and digested sludge dewatering. The daily usage is 757 cubic meters of diluted polymer with 0.22% of active ingredient (3% is the active ingredient percentage in the undiluted polymer emulsion). About 70% of the Mannich polymer is used for digested sludge dewatering and 30% for WAS and PS thickening. An anionic polymer is used in primary treatment to aid coagulation. The daily usage is 280 cubic meters of 3% active ingredient solution, diluted to 0.03% before injection.

### 3.1.3 Standards, reagents, solvents and filters

All purchased solvents (methanol, methylene chloride) were HPLC grade or superior, obtained from Fisher Scientific and used without further purification. Tert-Butyl alcohol (TBA) (ACS reagent grade, Sigma-Aldrich) was used as  $\cdot\text{OH}$  radicals scavenger. Potassium indigotrisulfonate, *N,N*-dimethylformamide, dimethylamine hydrochloride, uridine, sodium hydroxide, sodium phosphate monobasic monohydrate, sodium phosphate

dibasic heptahydrate (ACS reagent grade), phosphoric acid (ACS reagent grade,  $\geq 85$  wt. % in  $\text{H}_2\text{O}$ ) and hydrogen peroxide (50 wt. % in  $\text{H}_2\text{O}$ ) were purchased at  $>98\%$  purity from Sigma-Aldrich. Sodium sulfate anhydrous (Granular, ACS reagent grade), hydrochloric acid, ammonium chloride and sodium thiosulfate crystalline ( $> 99\%$  purity) were obtained from Fisher Scientific.  $1000 \text{ mg/L Br}^-$  in water, prepared with high purity NaBr and water was purchased from Sigma-Aldrich.

N-Nitrosodimethylamine (*d6*, 98%) from Cambridge Isotope Laboratories (Andover, MA) was used as a surrogate, N-Nitroso-Di-N-Propylamine (*d14*, 98%) from Cambridge Isotope Laboratories (Andover, MA) was used as an internal standard, and nitrosamine mix from Supelco (Bellafonte, PA) was used as the standard for NDMA analysis. Whatman (Clifton, NJ) glass microfiber filters grade GF/F ( $0.7 \mu\text{m}$  pore size) were used for filtering. Hypochlorite solution and polymer emulsions were given by facility's lab staff of the investigated wastewater treatment plant. 3% was the active ingredient percentage in all the polymer emulsions.

## 3.2 ANALYTICAL METHODS

### 3.2.1 TOC, inorganic constituents, and spectroscopic measurements

For TOC analysis, samples were acidified to  $\text{pH} < 3$  with hydrochloric acid and a Shimadzu total carbon analyzer was used for quantification. UV absorbance spectra were measured using a Cary Eclipse UV spectrophotometer. Fluorescence excitation-emission matrix (EEM) measurements were conducted using a Cary Eclipse fluorometer that employed a xenon excitation source. Excitation wavelengths were incrementally increased from 200 to 450 nm at 5 nm steps and for each excitation wavelength, the emission at longer wavelengths was detected at 1 nm steps. Data processing in Matlab included corrections for Raman scattering by subtracting emission of the blank and corrected for inner-filter effect (MacDonald et al, 1997). Regional integration was performed according to published literature (Chen et al., 2003; Gerrity et al., 2011). All the samples were  $0.7 \mu\text{m}$  filtered before UV and fluorescence analysis. Residual total chlorine was measured using a Hach DPD kit and residual dis-

solved ozone concentration was measured by indigo method (Rakness et al., 2010). Analysis of other inorganic water constituents was performed by the water reclamation facility's lab according to standard methods (APHA, 1998).

### 3.2.2 NDMA analysis

The NDMA analysis was performed using a modified version of EPA Method 521 (Munch and Basset, 2004). Briefly, analytes and the surrogate analyte were extracted by passing a 0.5 L water sample through a solid phase extraction (SPE) cartridge containing 2 g of 80-120 mesh coconut charcoal (UCT Enviroclean 521). The organic compounds were eluted from the solid phase with 12 mL of methylene chloride. Residual water was removed from the extracts by passing through five grams anhydrous sodium sulfate. Eluent was then concentrated under a gentle stream of nitrogen to 1.0 mL and the internal standard was added. Analysis of NDMA were performed on an Agilent 7000 Triple Quadrupole GC/MS-MS. The sample components were separated, identified, and measured by injecting 5  $\mu$ L of the concentrated extract onto the fused silica capillary column of the GC/MS-MS system equipped with Gerstel autosampler, and operated in the chemical ionization (CI) mode with ammonia as the reagent gas. Identification and quantitation were performed in the MS-MS mode with a resulting method reporting limit in ultrapure water of less than 1 ng/L.

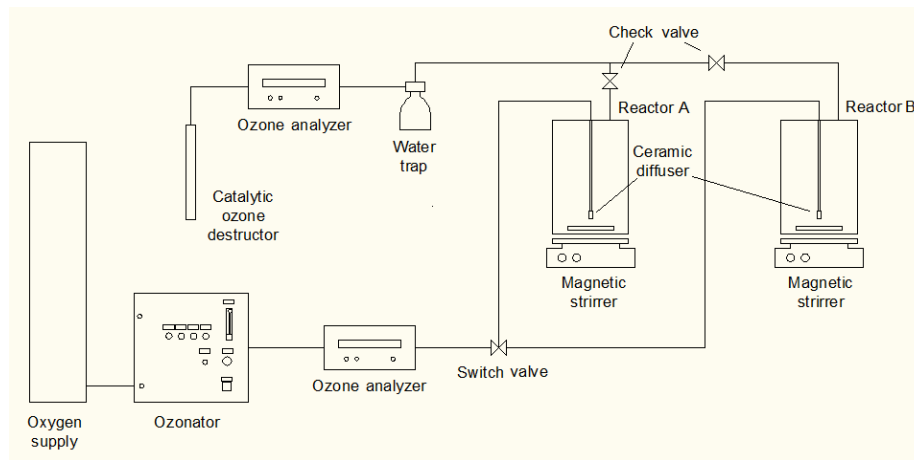
Other aspects of this analysis are described in Kahl et al. (2013).

## 3.3 EXPERIMENTAL METHODS

### 3.3.1 Bench scale ozonation

Ozone gas generated from pure oxygen using an ozone generator (Wedeco, Modular 4 HC series, Herford, Germany) was introduced into a glass reaction vessel containing the sample by a ceramic diffuser. Mixing was accomplished by a magnetic stirrer. The ozonation conditions were as follows: sample volume, 1 L; ozone concentration in feed gas, 12 mg/L; ozone gas flow rate, 1 L/min; temperature, 20 °C. Two glass reac-

tion vessels were set in parallel, one was filled with sample and the other one with DI water. Initially, ozone gas was bubbled into the glass jar with DI water in order to set the desired ozonation condition, then the ozone feed gas was deviated to the jar containing the sample by a switch valve. Ozone feed gas concentration and ozone off-gas concentration were measured by two pressure and temperature compensated ozone analyzers with UV quartz cells. The scheme of the utilized ozone system is shown in Figure 3.5.



**Figure 3.5** Lab-scale apparatus used for semi-batch ozonation

Over the whole experiments, ozone concentration data of the feed gas and off gas were recorded every 30 seconds and the applied ozone dose was calculated by mass balance:

$$\text{ozone dose} = \frac{Q_{\text{gas}} \cdot t \cdot (\beta_{\text{feed gas}} - \beta_{\text{off gas}})}{V}$$

where  $Q_{\text{gas}}$  is the gas flow,  $t$  is the time,  $\beta_{\text{feed gas}}$  and  $\beta_{\text{off gas}}$  are the ozone concentration in the feed gas and in the off gas, respectively, and  $V$  is the sample volume.

Experiments in deionized water (DI water) were buffered by 2.5 mM phosphate buffer and sodium hydroxide was added to reach the desired pH.

### 3.3.2 Bench scale ultraviolet irradiation

Ultraviolet experiments using DMF solutions were carried out in bench scale low pressure UV (LPUV) collimated beam device (Wedeco, Herford, Germany). The DMF concentration in Milli-Q water was 2.5 mg/L. Ammonia was added for a final concentration of 4 mg/L as N and the pH was adjusted to 8 by 2.5 mM phosphate buffer. UV fluence ( $\text{mJ}/\text{cm}^2$ ) was determined by uridine actinometry (Jin et al., 2006) using identical geometry and solution volumes as in photolysis experiments. In a typical photolysis experiment, 500 mL of sample was placed in a  $125 \times 65$  mm crystallization dish (solution depth approximately 5 cm, open to the atmosphere). UV doses of 250, 500 and  $1000 \text{ mJ}/\text{cm}^2$  were applied with and without 3 mg/L of  $\text{H}_2\text{O}_2$  addition. After UV irradiation  $\text{NaClO}$  was added to achieve a  $\text{Cl}_2$  concentration of 4 mg/L and it was quenched by sodium thiosulfate after 3 hours of reaction time. Ammonia and  $\text{H}_2\text{O}_2$  concentration, chlorine dose, reaction time and pH simulated the full scale experiments at West basin WWRP described in section § 3.3.3. A control experiment was performed at the same experimental conditions but without UV or UV/ $\text{H}_2\text{O}_2$  treatment.

### 3.3.3 Sampling and full-scale experiments

Several campaigns of full-scale experiments were performed at West Basin WWRP (El Segundo (Los Angeles), California (USA)).

During the first campaign of experiments, water samples were collected at different point of the IPR system, including before RO (denoted as “Pre RO”), after RO (denoted as “Post RO”) and after UV/AOP reactor (denoted as “Post UV/ $\text{H}_2\text{O}_2$ ”) (this last sample was collected after lime addition but before chlorine disinfection). Samples from the first campaign collected in 20 liter containers with spigot were not further amended. Additionally, two amber glass bottles (1 L size) were collected directly from the process for each sampling point and immediately quenched in situ with 80 mg/L of sodium thiosulfate (denoted as “day 0”).

During the second campaign, samples were collected after the full scale UV/AOP treatment at two different UV doses and with and without 3 mg/L of hydrogen peroxide feed injected before the UV system (denoted as “UV half dose w/  $\text{H}_2\text{O}_2$ ”, “UV half dose w/o  $\text{H}_2\text{O}_2$ ”, “UV usual dose w/  $\text{H}_2\text{O}_2$ ”, “UV usual dose w/o  $\text{H}_2\text{O}_2$ ”). Indeed, as previous-

ly described, the UV system at the WWRP consists of four identical reactors connected in series and sampling points are present between the second and third reactor and after the last reactor (Figure 3.2). An ample purge time to clear the reactors residual hydrogen peroxide was provided to repeat the collection without hydrogen peroxide feed. The delivered UV dose of the ultraviolet disinfection and oxidation system was not given from lab's facility staff. Collection of the ozone-MF-RO pilot system effluent was also performed (denoted as "Pilot system effluent"), where ozone dose of around 10 mg/L was applied. Samples collected in 20 liters containers were promptly amended by sodium hypochlorite and lime in order to reach a final chlorine concentration of around 4 mg/L and pH 8 (i.e. the final stabilization and disinfection that take place at the WWRP were simulated). The effluent of the pilot system was amended only with lime because of the high chlorine residual present in the water. In addition, 1 L amber bottles were collected directly from the process for each collection event, these samples were not amended with chlorine and lime and were immediately quenched in situ by 80 mg/L of sodium thiosulfate (denoted as "day 0 not adjusted"). Finally, the final chlorinated effluent of the WWRP was also collected in 20 liters container (denoted as "Final effluent"); in this case no manipulation was needed. During the third campaign of collection, samples were collected before decarbonation tower (undecarbonated samples) (denoted as "Pre decarbonation") and immediately after decarbonation tower (completely decarbonated samples) (denoted as "Post decarbonation"). In addition, two 20 liters containers of sample were collected after water by-passing the decarbonation tower rejoined the main stream. In this latter case, the direct lime addition in the process was shut down and it was waited for the system to purge before collecting. Samples were pH and chlorine adjusted as done during the previous campaign. Only one of the containers collected after water by-passing was pH adjusted by sodium hydroxide (NaOH) instead of lime (samples collected after water by-passing were denoted as "Lime addition" and "NaOH addition"). Even during this sampling campaign, 1 L amber bottles were collected directly from the process for each collection event and immediately quenched in situ by 80 mg/L of sodium thiosulfate without further manipulation ("day 0 not adjusted" samples).

For all the collection campaigns, the samples were shipped overnight to The University of Arizona (Tucson, AZ (USA)), where they were stored at room temperature (22 – 23 °C) and covered with aluminum foil to



protect the samples from light. Sub-sampling from the containers were performed after 1, 4, 7, 14 and 28 days of chlorine contact time (denoted as “day 1”, “day 4”, “day 7”, “day 14” and “day 28”, respectively) for the first and second campaign; sub-sampling were performed only after 1 and 4 days (denoted as “day 1” and “day 4”) during the third campaign. Triplicate subsamples for the first campaign and duplicates subsamples for the second and third campaign were collected in 1 L amber bottles and amended with 80 mg/L of sodium thiosulfate to quench any residual chlorine. With each daily aliquot, residual total chlorine and pH were always monitored. Furthermore, during the second and third campaign, sub-samplings from the containers were also performed at the WWRP and the sub-samples were quenched within 3 hours of the collection event (denoted as “day 0”).

Wastewater samples were collected at Hyperion WWTP too. Samples of Hyperion primary influent, primary effluent, secondary effluent (i.e. influent to West Basin WWRP), and pre-ozonated wastewater at the pilot plant were always collected as 24 hours composite samples, unless otherwise specified. Composite samples (24-hr) of the centrates from WAS thickening centrifuges and dewatering centrifuges also were collected. For this part of experiments, samples were shipped overnight to the laboratory and kept refrigerated at 4 °C until the ozonation tests.

Grab samples of wastewater final effluents were collected at three different plants in Tucson (Arizona (USA)): Roger Road WWTP, Ina Road WWTP, Green Valley WWTP. These wastewater effluents are used for different reuse typologies in Arizona (USA). Ozonated samples were collected at the pilot scale ozone/UV/H<sub>2</sub>O<sub>2</sub> reactor (Wedeco/ITT, Herford, Germany) in Green Valley. Roger Road and Ina Road effluents were ozonated at the laboratory by spiking aliquots of ozone stock solution from a batch reactor.



## 4 RESULTS AND DISCUSSION

### 4.1 NDMA FORMATION IN WASTEWATERS DESTINED FOR INDIRECT POTABLE REUSE

NDMA formation by ozonation was investigated in four different wastewater effluents destined for alternative reuse. The selected wastewaters present different water quality characteristics and two of them (Ina Road and Green Valley) are treated for nitrogen removal. Table 4.1 reports water quality parameters and the NDMA formation at different ozone doses normalized to the dissolved organic concentration (DOC). An ozone dose normalized to the DOC concentration has often been used as an operating parameter to compare waters with varying DOC concentration (Nakada et al., 2007).

**Table 4.1 NDMA formation during ozonation of different wastewater effluents**

Wastewater effluent	TN	DOC	O <sub>3</sub> /DOC	NDMA(ng/L)
Hyperion	48.7	14.3	0.0	55
Hyperion	48.7	14.3	0.3	154
Hyperion	48.7	14.3	0.7	227
Roger Road	39.5	10.5	0.0	17
Roger Road	39.5	10.5	0.1	26
Roger Road	39.5	10.5	0.3	35
Roger Road	39.5	10.5	0.5	46
Ina Road	8.2	5.3	0.0	5
Ina Road	8.2	5.3	0.2	8
Ina Road	8.2	5.3	0.6	9
Ina Road	8.2	5.3	0.9	10
Green Valley	2.4	5.4	0.0	1
Green Valley	2.4	5.4	0.3	1
Green Valley	2.4	5.4	0.6	1
Green Valley	2.4	5.4	1.1	4
Green Valley	2.4	5.4	1.7	4

*TN, total nitrogen. DOC, dissolved organic carbon. O<sub>3</sub>, ozone.*

NDMA formation was lower in effluents treated for nitrogen removal and only Green Valley effluent was always in compliance with potable

reuse requirements (CDPH, 2009b). Wastewater often contains significant concentrations of NDMA precursors (Krasner et al., 2009), and to produce water with NDMA levels lower than 10 ng/L often need the use of advanced technologies. Hyperion wastewater effluent presented a broadly larger NDMA formation than all the other wastewater. For this reason Hyperion wastewater was investigated in more detail in this study.

## **4.2 NDMA FORMATION AT WEST BASIN WWRP**

In this section NDMA formation along the treatment systems at West Basin reclamation plant was investigated. NDMA is produced due to the chlorine addition for organic fouling control of the membranes treatment and for the final disinfection. Particularly, the effect of the UV oxidation system on NDMA (re)formation during the following final disinfection was studied in detail. In addition, the effects of pre-ozonation and carbon dioxide content in wastewater were also evaluated. Ozonation and AOPs (such as UV/H<sub>2</sub>O<sub>2</sub>) are gaining always more popularity in water reuse application, and the study of their effect on carcinogenic DBPs formation and control has critical importance.

### **4.2.1 NDMA formation along the treatment train**

Table 4.2 reports the obtained results from the first campaign of full-scale experiments at West Basin where NDMA formation was investigated along the treatment train of the WWRP. NDMA concentration in the RO feed water containing chloramines was initially 26 ng/L, which reached a maximum concentration of 248 ng/L by day 14. The concentration did not increase by day 28, likely due to essentially complete consumption of total chlorine. Higher initial chlorine doses, or subsequent chlorine addition, probably would have increased the observed NDMA concentrations. In the RO permeate water NDMA concentration started at 13 ng/L and increased to 24 ng/L within 24 hours. After 24 hours, there was no significant increase in NDMA despite a continued chlorine residual through 14 days. The lack of additional NDMA formation beyond 24 hours suggests that precursors present in RO permeate were fully consumed within 24 hours of contact time.

**Table 4.2 NDMA formation after 0, 1, 4, 7, 14 and 28 days of chlorine contact time at West Basin WWRP, before reverse osmosis (Pre RO), after reverse osmosis (Post RO) and after UV/H<sub>2</sub>O<sub>2</sub> treatment (Post UV/H<sub>2</sub>O<sub>2</sub>)**

Constituent	Day 0	Day 1	Day 4	Day 7	Day 14	Day 28
<b>Pre RO</b>						
NDMA (ng/L)	26 (0.2) <sup>a</sup>	35 (0.6)	158 (0.7)	232 (7.3)	248 (7.2)	216 (6.9)
Total Cl <sub>2</sub> (mg/L)	2.9	1.3	0.6	0.2	0.1	0.1
pH	6.4	6.8	6.7	6.8	7.1	7.0
<b>Post RO</b>						
NDMA (ng/L)	13 (0.1)	24 (0.2)	25 (1.7)	22 (0.4)	25 (7.2)	21 (0.3)
Total Cl <sub>2</sub> (mg/L)	3.9	3.9	3.9	3.5	2.2	0.5
pH	5.5	6.0	5.7	6.1	6.3	7.8
<b>Post UV/ H<sub>2</sub>O<sub>2</sub></b>						
NDMA (ng/L)	4	6 (0.2)	6 (0.2)	5 (0.1)	6 (1.9)	5 (0.1)
Total Cl <sub>2</sub> (mg/L)	1.1	0.7	0.3	0.3	0.2	0.1
pH	8.0	8.3	8.2	8.4	8.4	8.2

<sup>a</sup> ( $\pm$  one standard deviation of the measurement derived from the standard curve).

These data confirm that RO removes the vast majority of NDMA precursors in agreement with previous studies (Mitch and Sedlak, 2004; Krauss et al., 2010). In post-UV/H<sub>2</sub>O<sub>2</sub> water, the NDMA level was initially 4 ng/L and did not increase significantly over the study. However, it is noteworthy that chlorine levels were extremely low and it likely limited further NDMA formation. 50 % direct NDMA rejection by reverse osmosis was in agreement with literature data (Plumlee et al., 2008; Fujioka et al., 2012; Fujioka et al., 2013).

#### 4.2.2 UV dose and hydrogen peroxide effect on NDMA removal and reformation

As specified before, the UV system consists of four identical reactors connected in series and individual reactor performance can be considered additive. Samples for the experiments were collected between the second and third reactor and after the last reactor. Thus, the UV dose delivered after four reactors is the usual dose at WWRP, the UV dose delivered after two reactors is half of the usual UV dose of the ultraviolet system. UV doses for NDMA attenuation are generally very high and Sharpless and Linden (2003) reported that a UV fluence of  $\sim 1000$  mJ/cm<sup>2</sup> is required for a log order reduction in NDMA. During this phase of the study, the final effluent of the WWRP (i.e. the effluent after

decarbonation and final stabilization and disinfection) was also collected for NDMA analysis. The differences between the final effluent and the sample collected after the fourth UV reactor during  $H_2O_2$  feeding were the  $CO_2$  concentration in water and the amount of lime added to adjust the pH to 8. Indeed, water passed through decarbonation towers has a lower  $CO_2$  content and it needs less amount of lime for stabilization. Experiments findings showed that both the addition of  $H_2O_2$  and lower UV dose resulted in decreased attenuation of NDMA (day 0 not adjusted samples in Table 4.3 and Figure 4.1).

**Table 4.3** NDMA formation after 0, 1, 4, 7, 14 and 28 days of chlorine contact time after UV and UV/ $H_2O_2$  treatment with two UV doses (usual dose and half dose at West Basin) using the full scale reactor. Final effluent, sample collected after normal UV/ $H_2O_2$  treatment, decarbonation, lime stabilization and final chlorination. Day 0 not adj., day 0 not adjusted (samples not amended with chlorine and lime)

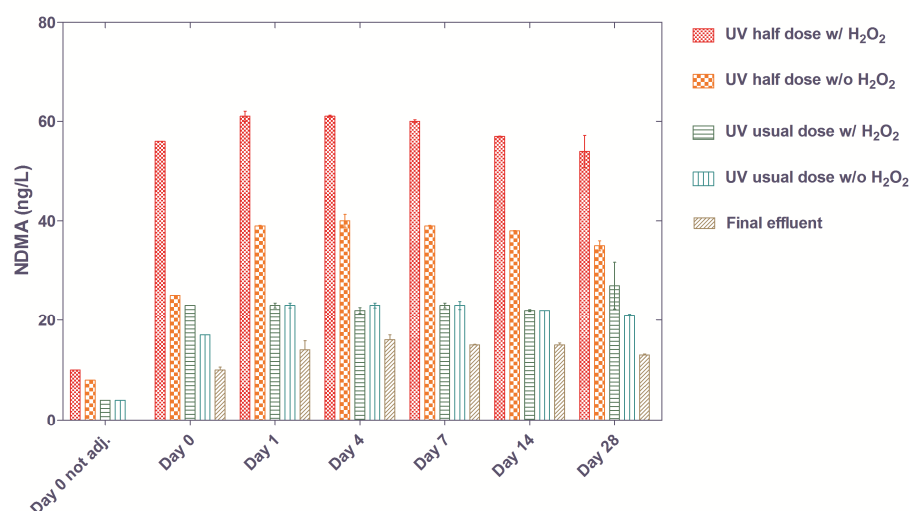
Constituent	Day 0 not adj.	Day 0	Day 1	Day 4	Day 7	Day 14	Day 28
<b>UV half dose w/o <math>H_2O_2</math></b>							
NDMA (ng/L)	8	25	39 (0.1) <sup>a</sup>	40 (1.3)	39 (0.1)	38 (0.1)	35 (1.0)
Total $Cl_2$ (mg/L)	2.3	4.5	3.4	3.2	3.2	3.1	2.1
pH	5.8	8.0	8.4	8.3	8.5	8.4	8.4
<b>UV half dose w/ <math>H_2O_2</math></b>							
NDMA (ng/L)	10	56	61 (1.0)	61 (0.2)	60 (0.3)	57 (0.1)	54 (3.2)
Total $Cl_2$ (mg/L)	2.3	4.1	3.5	3.1	2.8	2.5	1.1
pH	5.8	8.2	8.6	8.6	8.5	8.5	8.6
<b>UV usual dose w/o <math>H_2O_2</math></b>							
NDMA (ng/L)	4	17	23 (0.5)	23 (0.5)	23 (0.8)	22 (0.1)	21 (0.2)
Total $Cl_2$ (mg/L)	1.0	4.0	3.7	3.5	3.5	3.2	2.6
pH	5.6	8.0	8.4	8.3	8.5	8.4	8.4
<b>UV usual dose w/ <math>H_2O_2</math></b>							
NDMA (ng/L)	4	23	23 (0.5)	22 (0.6)	23 (0.5)	22 (0.2)	27 (4.7)
Total $Cl_2$ (mg/L)	1.1	4.3	3.6	3.1	2.8	2.6	1.5
pH	5.6	8.2	8.7	8.7	8.6	8.5	8.6
<b>Final effluent</b>							
NDMA (ng/L)	-	10 (0.6)	14 (1.8)	16 (1.0)	15 (0.1)	15 (0.4)	13 (0.2)
Total $Cl_2$ (mg/L)	-	4.4	3.8	3.5	3.2	3.0	2.2
pH	-	8.0	8.5	8.6	8.6	8.4	8.2

<sup>a</sup> ( $\pm$  one standard deviation of the measurement derived from the standard curve).

The  $\text{H}_2\text{O}_2$  effect on NDMA photolysis is likely due to the absorption/screening of UV light which lowers the number of photons reaching NDMA molecules. In agreement, Sharpless and Linden (2003) predicted by mathematical model that light-screening by  $\text{H}_2\text{O}_2$  may decrease the NDMA removal rates for optical path lengths typical of those found in UV reactors. No difference in initial NDMA concentration (day 0 not adjusted samples) (Table 4.3) was observed from samples treated by full UV dose with and without  $\text{H}_2\text{O}_2$  addition. Both values were 4 ng/L and absorption/screening of UV light by  $\text{H}_2\text{O}_2$  didn't affect the NDMA photolysis at this high UV dose. When chlorine was added and the pH adjusted to 8, NDMA concentration rose in all the samples. As shown in Table 4.3, NDMA formation reached 56 ng/L within 3 hours (day 0) and 61 ng/L within 24 hours (day 1) in sample treated with low UV dose and 3 mg/L of  $\text{H}_2\text{O}_2$ . Sample treated with low UV dose and without hydrogen peroxide had a lower NDMA concentration, 25 ng/L after 3 hour of chlorine contact time (day 0) and 39 ng/L after 24 hours (day 1). To the contrary, samples treated with high UV dose and with and without  $\text{H}_2\text{O}_2$  addition showed similar trend. NDMA was found at 17 ng/L (day 0) and 23 ng/L (day 1) in sample without  $\text{H}_2\text{O}_2$  and 23 ng/L (day 0) in sample with  $\text{H}_2\text{O}_2$ . NDMA concentration remained stable over 28 days later in all the samples despite chlorine residual was still present over the same time period. Thus, different UV doses and  $\text{H}_2\text{O}_2$  affected the NDMA reformation during post-chloramination. In addition, residual total chlorine measurements suggest that chloramines consumption was essentially not impacted by  $\text{H}_2\text{O}_2$  presence, according to the slow rate constant for the reaction between  $\text{H}_2\text{O}_2$  and monochloramine ( $2.76 \times 10^{-2} \text{ M}^{-1}\text{s}^{-1}$ ), and  $\text{H}_2\text{O}_2$  and dichloramine ( $3.60 \times 10^{-6} \text{ M}^{-1}\text{s}^{-1}$ ) (McKay et al., 2013).

$\text{H}_2\text{O}_2$  can have two different effects on NDMA reformation: (1) absorption/screening of UV light may affect the NDMA precursors photolysis, (2) degradation by-products formed during UV/ $\text{H}_2\text{O}_2$  treatment may have higher NDMA formation rate compared to the parent compounds during chloramination. No studies supporting the first hypothesis are present in literature, whereas several studies have reported results in agreement with second hypothesis. In these studies, degradation products of the pharmaceuticals tramadol, doxylamine and diltiazem were shown to have a higher NDMA FP than the correspondent parent compound (Chen et al., 2011; Redjenovic et al., 2012; Farré et al., 2012). Furthermore, researchers reported that even the only UV irradiation is

able to enhance the NDMA formation through more reactive degradation by-products production (Redjenovic et al., 2012; Soltermann et al., 2013). Particularly, Soltermann et al. (2013) hypothesized N-Nitrosamine formation in pool water to occur via the reaction of nitric oxide or peroxynitrite with the secondary aminyl radical, which are products from the photolysis of monochloramine and chlorinated secondary amines, respectively. Among the pharmaceuticals tramadol, doxylamine and diltiazem, only degradation products of tramadol, subjected to UV irradiation without peroxide, were reported to have an enhanced NDMA FP (Redjenovic et al., 2012). In general, the enhanced NDMA formation resulted depended on UV dose, precursors and  $\text{H}_2\text{O}_2$  concentration, and sometimes extended oxidations reduced the final NDMA reformation due to the further oxidation of the more reactive by-products (Chen et al., 2011; Redjenovic et al., 2012; Farré et al., 2012; Soltermann et al., 2013). This is the first study to report an enhanced NDMA formation in a wastewater used for indirect potable reuse after a full scale UV/AOP treatment.



**Figure 4.1** NDMA formation after 0, 1, 4, 7, 14 and 28 days of chlorine contact time after UV and UV/ $\text{H}_2\text{O}_2$  treatment with two UV doses (usual dose and half dose at West Basin) using the full scale reactor. Final effluent, sample collected after normal UV/ $\text{H}_2\text{O}_2$  treatment, decarbonation, lime stabilization and final chlorination. Day 0 not adj., day 0 not adjusted (samples not amended with chlorine and lime)



In regard to the final effluent analysis, it was found that this water initially presented a concentration of NDMA of 10 ng/L that increased to 14 ng/L within 24 hours (day 1) and to 16 ng/L by day 4. Not clear are the differences of NDMA concentration (more than 10 ng/L after 24 hours) between this effluent and the sample collected after the UV reactor and treated by full UV dose and  $\text{H}_2\text{O}_2$ . As mentioned before a different  $\text{CO}_2$  content or a different amount of lime added may be the reason of the found difference in NDMA formation. It is noteworthy to highlight that Lv et al. (2007) in a theoretical study on NDMA formation reported that at pH higher than 7 NDMA can be formed from DMA reacting with nitrite anion in the presence of carbon dioxide, which may catalyze the reaction. The possible  $\text{CO}_2$  and lime contribution were better investigated later in the present study (§ 4.2.4).

In any case, the NDMA reformation by chloramination after UV/ $\text{H}_2\text{O}_2$  treatment produced values not in compliance with water reuse requirements (OMOE, 2004; CDPH, 2009b).

#### 4.2.3 Impact of pre-ozonation on NDMA formation

Ozonation of the influent to the pilot system produced elevated amount of NDMA and 227 ng/L was the initial concentration in the pilot effluent (i.e. RO permeate) (day 0 not adjusted, Table 4.4). The NDMA production during ozonation can be assumed even higher in raw water considering partial NDMA rejection by RO membrane. After lime addition and pH adjustment from 5.6 to 8, the NDMA concentration increased to 287 ng/L within 3 hours. The residual chlorine after RO treatment was 5.5 mg/L, no more chlorine was added and the NDMA rise can be considered due to only pH increase. In agreement, several studies showed that NDMA formation from chloramination of surface water and selected compounds, including DMA, diuron and ranitidine, increased with pH with a maximum formation rate between pH 7 and 9 (Mitch et al., 2003a; Schreiber and Mitch, 2006a; Chen and Young, 2008; Le Roux et al., 2011). NDMA concentrations in samples held for longer times were relatively stable, despite the high chlorine residual in water, before decreasing to 233 ng/L in the 28 day sample.

Further ozonation experiments were performed at bench scale in laboratory utilizing the influent to West Basin WWRP. Wastewater ozonations were performed using ozone doses of 5 mg/L and 10 mg/L and with and without 10 mg/L of chlorine addition post-ozonation in order to

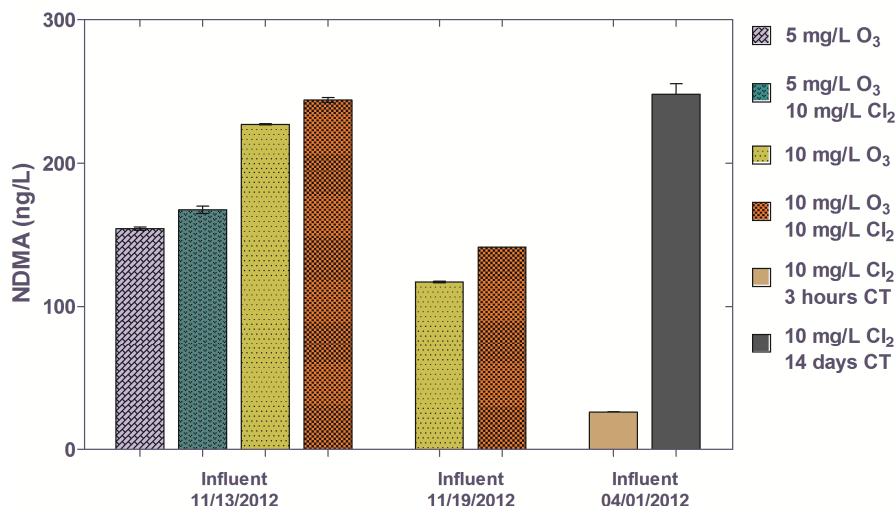
simulate the operation conditions of the pilot system at West Basin. The addition of chlorine lead to formation of chloramines because of the elevated ammonia load present in the water (Table 3.2). Chlorine residual was quenched after three hours of contact time by sodium thiosulfate. Because of water quality variability, flow rate variability and instability of the ozone generator, the transferred ozone dose from the pilot system to wastewater was observed to range from 3 mg/L to 12 mg/L. Thus, ozone doses of 5 and 10 mg/L can be considered as representative of the ozonation conditions at the pilot system.

**Table 4.4 NDMA formation after 1, 4, 7, 14 and 28 days of chlorine contact time in the pilot system effluent. Day 0 not adj., day 0 not adjusted (samples not amended with lime)**

Constituent	Day 0 not adj.	Day 0	Day 1	Day 4	Day 7	Day 14	Day 28
<i>Pilot system effluent</i>							
NDMA (ng/L)	227	287	279 (3.6) <sup>a</sup>	282 (0.1)	278 (4.4)	262 (0.7)	233 (5.3)
Total Cl <sub>2</sub> (mg/L)	5.5	5.5	4.7	4.3	3.9	3.6	2.6
pH	5.6	8.1	8.4	8.5	8.5	8.4	8.4

<sup>a</sup>(± one standard deviation of the measurement derived from the standard curve)

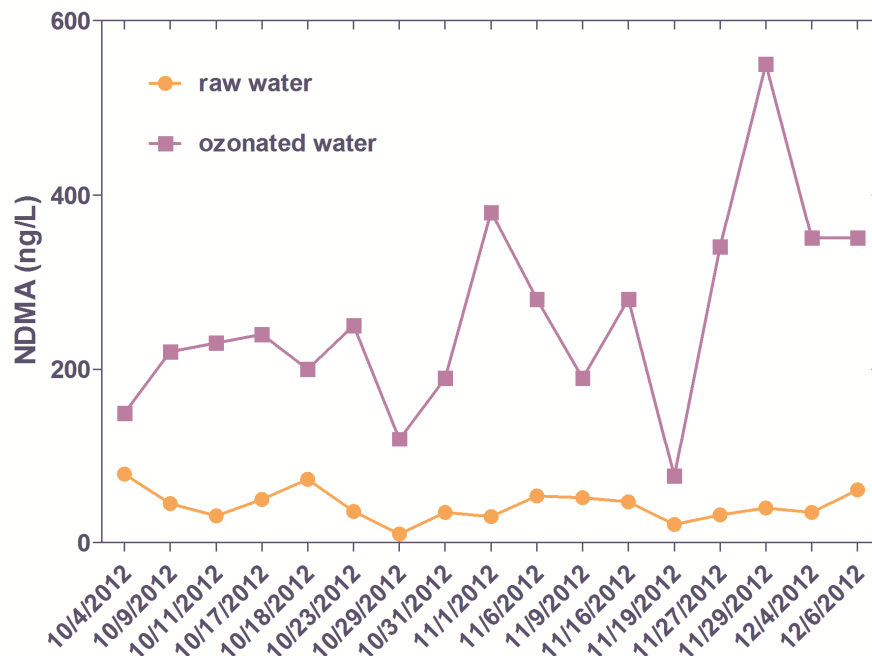
A very high and rapid NDMA formation by ozone was evident and it depended on the applied ozone doses (Figure 4.2). Indeed, a higher ozone dose resulted in a higher NDMA production and the dissolved ozone residual in water was always zero due to the high instantaneous ozone demand (IOD) common for wastewater (Wert et al., 2007). Furthermore, in samples collected at different times, the same ozone dose produced different amounts of NDMA, showing a high temporal variability of NDMA precursors concentration in the studied wastewater effluent. Noteworthy is that the sample collected on November 13 is a 24-hour composite and it takes into account the daily variation of water characteristics; instead the sample collected on November 19 is only a grab sample. Post-chloramination after ozonation at different ozone doses resulted always in a slight increase of NDMA. NDMA formation by ozonation in Figure 4.2 is compared to the NDMA formation by chloramination observed during the first campaign of full-scale experiments in Pre-RO samples.



**Figure 4.2** NDMA formation upon ozonation, ozonation with post-chlorination and chlorination alone in West Basin WWRP influent. Post ozonation Chlorine addition was quenched after 3-h. CT, contact time. Error bars represent the standard deviation of experimental duplicates

During the mentioned experiments, chlorine produced 26 ng/L of NDMA after around 3 hours contact time and a chlorine residual of 2.9 mg/L was still present in water. Complete chlorine depletion occurred only after 14 days of contact time, when the NDMA concentration rose to 248 ng/L. Long reaction times (i.e. several days of contact time) are unlikely observed at a WWRP and thus this NDMA concentration by chloramination is generally unrealistic. Within the WWRP studied, three hours is a common chlorine contact time.

The high variability in NDMA formation upon ozonation observed at West Basin from October to December 2012 is showed in Figure 4.3. The high amount of NDMA produced during ozonation results difficult to lower to required concentration for potable reuse (OMOE, 2004; CDPH, 2009b) and it will need elevated energy consumption in a following UV treatment for a substantial photo-degradation.



**Figure 4.3** NDMA formation observed at West Basin in ozonated wastewater samples collected from October to December 2012

In the presented case study, pre-ozonation resulted an inconvenient process for NDMA control in water reuse application.

#### 4.2.4 Carbon dioxide and lime effect on NDMA formation

All the samples collected during the third campaign of full-scale experiments had very similar NDMA results. No immediate NDMA increase was evident in all the samples after chlorine addition and pH correction (day 0 samples, Table 4.5). NDMA rose to 7 – 8 ng/L after 24 hours, but remained stable later and always lower than 10 ng/L. No impact from decarbonation or lime addition was evident. Lime formed no more NDMA than did sodium hydroxide, so the NDMA formation is not related to the lime used in the full scale process. Likely, a less concentration of precursors was present in this water compared to the water collected during the second campaign of full-scale experiments. NDMA monitoring at the WWRP only occasionally detected NDMA concentration in the final product higher than 10 ng/L (not published data), prob-

ably due to the variable quality of the water and RO membrane conditions and performance.

**Table 4.5** NDMA formation after 0, 1 and 4 days of chlorine contact time. Pre decarbonation, sample collected before decarbonation tower. Post decarbonation, sample collected after decarbonation tower. Lime addition, sample stabilized by lime. NaOH addition, sample stabilized by sodium hydroxide. Day 0 not adj., day 0 not adjusted (samples not amended with chlorine, lime or sodium hydroxide)

Constituent	Day 0 not adj.	Day 0	Day 1	Day 4
<b>Pre decarbonation</b>				
NDMA (ng/L)	2	3 (0.1) <sup>a</sup>	7 (0.9)	7 (0.1)
Total Chlorine (mg/L)	1.1	4.5	2.9	1.7
pH	5.8	8.0	8.1	8.4
Alkalinity (mg/L as CaCO <sub>3</sub> )	19	73	-	-
Total CO <sub>2</sub> (mg/L)	77	65	-	-
<b>Post decarbonation</b>				
NDMA (ng/L)	3	4 (0.2)	7 (0.9)	8 (1.1)
Total Chlorine (mg/L)	1.1	4.3	3.1	1.7
pH	7.8	8.2	8.6	8.6
Alkalinity (mg/L as CaCO <sub>3</sub> )	21	24	-	-
Total CO <sub>2</sub> (mg/L)	19	21	-	-
<b>Lime addition</b>				
NDMA (ng/L)	5	5 (1.2)	8 (0.9)	7 (0.1)
Total Chlorine (mg/L)	1.1	4.3	3.0	1.5
pH	n.a.	8.0	8.2	8.4
<b>NaOH addition</b>				
NDMA (ng/L)	5	4 (0.2)	8 (0.4)	8 (0.1)
Total Chlorine (mg/L)	1.1	4.0	3.3	1.8
pH	n.a.	8.1	8.3	8.5

na=not available; <sup>a</sup> ( $\pm$  one standard deviation of the measurement derived from the standard curve).

At pH 8 carbon dioxide is mainly present in the form HCO<sub>3</sub><sup>-</sup>. The difference in carbon dioxide concentration between pre-decarbonation and post-decarbonation water is evident from the different measured values of alkalinity and total carbon dioxide (Table 4.5). Probably, the low precursors concentration and water quality may also have affected the carbon dioxide catalyzing effect on NDMA production.

### 4.3 PRECURSORS SOURCE IDENTIFICATION

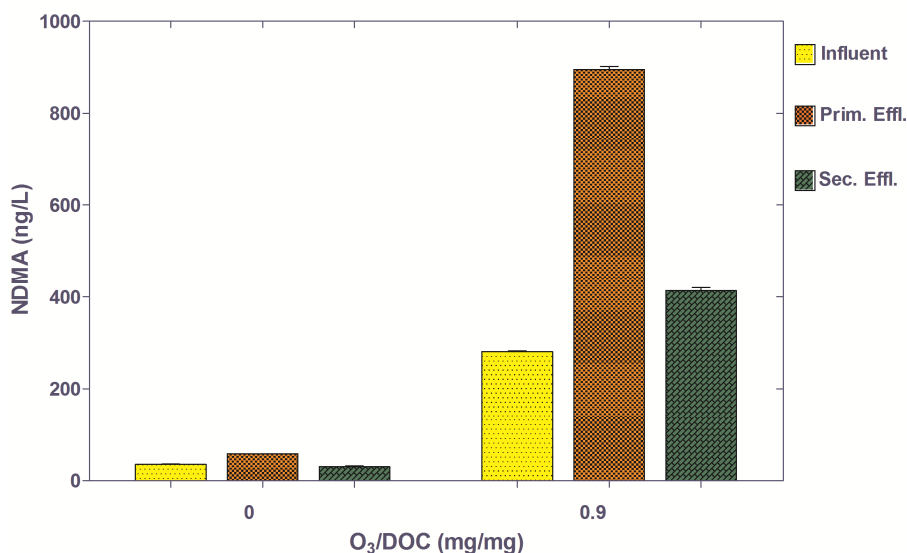
Different ozonation tests were performed using wastewater collected at different point at Hyperion WWTP in order to figure out the source of NDMA precursors. In this section are reported the results of the accomplished investigation. Polymers and recycle streams were tested to assess their potential for NDMA formation. The role of inorganic water constituents (i.e. ammonia and bromide) on NDMA formation during ozonation was also evaluated and new formation pathways are proposed.

#### 4.3.1 Hyperion wastewater ozonation

In order to identify the source of NDMA precursors upon ozonation of the investigated wastewater, different ozonation tests were performed. Primary influent, primary effluent, and secondary effluent of Hyperion WWTP collected the same day were tested to clarify if most of NDMA precursors are present in the raw influent or are produced within the WWTP. All the tested samples were filtered at 0.7  $\mu\text{m}$  and ozonated using the same ozone to DOC ratio (0.9 mg  $\text{O}_3$ /mg DOC).

The ozonation of Hyperion WWTP influent showed that some NDMA precursors enter the WWTP from the sewage streams; however, most production of NDMA was observed in the primary effluent (Figure 4.4). This suggests that either the precursors entering with the raw sewage are transformed within the plant or that chemicals added during the primary process and/or the sludge treatments are contributing to the increased NDMA formation observed.

In regard to NDMA concentration without ozone, the highest value was also found in the WWTP primary effluent. Duplicate measurements of NDMA yielded concentrations of 35 ng/L ( $\pm 0.5\%$ ), 58 ng/L ( $\pm 0.03\%$ ) and 30 ng/L ( $\pm 1.3\%$ ) in primary influent, primary effluent, and secondary effluent, respectively. Biological treatment resulted in a 47% reduction of NDMA.



**Figure 4.4** NDMA concentration in ozonated and not ozonated primary influent (Influent), primary effluent (Prim. Effl.) and secondary effluent (Sec. Effl.) of Hyperion WWTP. Ozonated samples were analyzed in triplicate, whereas not ozonated samples were analyzed in duplicate. Error bars represent one standard deviation of the measurement derived from the standard curve

Since the primary effluent had a higher NDMA concentration than the raw sewage, it is likely that centrate streams returned to the primary clarifier are contributing to the elevated NDMA observed.

#### 4.3.2 Polymers and recycle streams test

At Hyperion WWTP an anionic polymer is used in primary treatment to aid coagulation and a cationic Mannich polymer is employed for digested sludge dewatering and for WAS and PS thickening. To verify the polymer contribution to NDMA production, 3 mg/L as active ingredient of the given polymer emulsions were spiked in the secondary effluent and ozonated at 11 mg/L O<sub>3</sub>. The polymers ozonation was also tested in DI water buffered at pH 8, where 11 mg/L O<sub>3</sub> was applied to polymer solutions with a concentration of 10 mg/L as active ingredient and the ozone residual was quenched by sodium thiosulfate within 30 seconds. Table 4.6 reports the net amount of NDMA produced during ozonation of anionic and Mannich polymer solutions. No increased NDMA forma-

tion was observed after anionic polymer spike, whereas significant NDMA production occurred when Mannich polymer was ozonated.

Around 0.1 mg/L as active ingredient is the dosed concentration of anionic polymer in the primary clarifier at Hyperion WWTP and is noteworthy to consider that only trace levels of polymer will persist in water after the coagulation/sedimentation process, as most of polymer will remain attached to the sludge (Park et al., 2009a).

Different considerations are needed for the cationic Mannich polymer used for sludge thickening and dewatering operations due to the very high dosages of polymer applied. Aminomethylated polyacrylamide, generally referred to as Mannich polymer, is made by the attachment of aminomethylated tertiary amine to already-prepared polyacrylamide backbone using DMA and formaldehyde via Mannich reaction followed by acidification (Figure 4.5).

**Table 4.6 NDMA formation from anionic polymer and Mannich polymer**

Water matrix	Polymer	Polymer (mg/L as a.i. <sup>a</sup> )	O <sub>3</sub> (mg/L)	NDMA (ng/L)	NDMA (ng/mg) <sup>c</sup>
Wastewater effluent	Anionic	3	11	ND <sup>b</sup>	-
Wastewater effluent	Mannich	3	11	126	42
DI water	Anionic	10	11	ND	-
DI water	Mannich	10	11	1044	104

<sup>a</sup> a.i., active ingredient. <sup>b</sup> ND, not detectable. <sup>c</sup> Produced amount of NDMA divided by the polymer active ingredient concentration to yield units in ng NDMA per mg of polymer active ingredient.

Because the Mannich reaction is reversible, DMA and formaldehyde can be reproduced during usage or storage. Park et al. (2009a) tested the Mannich at different times of storage in the dark; significant hydrolysis of the polymer occurred yielding a high DMA concentration in the polymer solution. Furthermore, during NDMA FP tests by chloramination, an extremely high NDMA concentration was found and it was attributed to the elevated residual of DMA along with the unstable and relatively easy oxidizable structure of the Mannich polymer (Park et al., 2009a). This dimethylamine-based polymer was reported to produce approximately 400 times more NDMA per mol of nitrogen than dimethylamine, indicating that the polyacrylamide backbone somehow enhances



NDMA formation (Mitch and Sedlak, 2004). Degradation products of Mannich polymer such as DMA can be dissolved in the supernatant and not adsorbed in the sludge, thus this polymer can be considered as a source of secondary amines or other NDMA precursors entering the primary clarifiers.

Following this rationale and in order to explore if the sludge treatment train and the related use of polymer affect the NDMA formation, the recycle streams entering the primary clarifiers were investigated. Centrates collected from the WAS thickening centrifuges and from the dewatering centrifuges were ozonated after 0.7  $\mu\text{m}$  filtration.

Very high NDMA formation was observed in both the ozonated centrates, especially from the stream after dewatering centrifuges (Table 4.7). This result can explain the high NDMA concentration in the ozonated primary effluent as well as the consideration that no other possible sources of NDMA precursors are connected to the primary clarifiers.

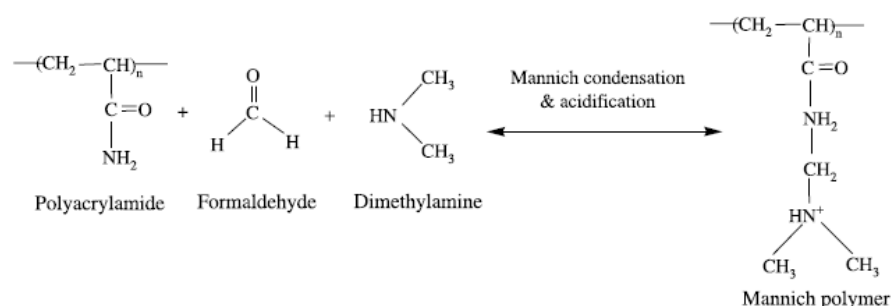


Figure 4.5 Synthesis of Mannich polymer (adapted from Park et al., 2009)

Even higher NDMA formation can be expected in the centrates at increased ozone dose, particularly considering the elevated load of dissolved solids typical of thermophilic digestion supernatant that can compete for ozone with the NDMA precursors. The fact that the NDMA formation in the recycle stream after the dewatering centrifuges is significantly higher than the NDMA formation in the centrate after WAS centrifuges is possibly due to the considerably higher Mannich polymer dosage in the dewatering centrifuge ( $\sim 100$  mg/L as active ingredient is used for sludge dewatering;  $\sim 2$  mg/L as active ingredient is used for WAS and PS thickening). Furthermore, an extremely high ammonia concentration typical of an anaerobic sludge digestion was measured in this

latter centrate (Table 4.7). A contribution to the NDMA formation may also come from biological degradation of hydrophobic compounds during anaerobic digestion but this assumption needs further researches to be confirmed. Padhye et al. (2009) found that NDMA precursors concentrations in sludge decreased after anaerobic digestion in two southeastern United States WWTPs, whereas it showed a 3-fold increase compared to WAS samples in a third plant, underlining the complexity of biological processes involved in sludge digestion and differences in sludge components.

In any case, the high NDMA formation obtained in both the investigated recycle streams seems to suggest that biological treatment may have a role on the degradation of polymers or other hydrophobic compounds entering the WWTP releasing more simple and highly reactive ozone NDMA precursors. Indeed, NDMA formation from polymers has reported to be strongly related to their degradation (Park et al., 2009b; Padhye et al., 2011) and some decomposition products have already been shown to high NDMA yields during ozonation (Schmidt and Brauch, 2008). Finally, the centrifuges used for sludge thickening and dewatering could facilitate the release in the supernatant of precursors still adsorbed in the sludge because of the forceful mixing.

A high NDMA concentration was also found in the non-ozonated dewatering centrate (568 ng/L), whereas a modest concentration was found in the WAS thickening recycle stream (50 ng/L). Previous studies (Keefer and Roller, 1973) have reported the formation of NDMA from DMA and nitrite. N-nitrosation reaction is most favorable at acid pH, but can be catalyzed by carbonyl compounds such as formaldehyde or formic acid at near neutral pH conditions. It has been proposed that formaldehyde catalyzes N-nitrosation by interacting with a secondary amine to form an adduct that is highly reactive toward nucleophilic attack by nitrite (Keefer and Roller, 1973).

The above rationale along with the elevated NDMA concentration observed in the dewatering centrate seems to confirm the degradability of the Mannich polymer and the subsequent release of DMA and formaldehyde in significant concentration into the supernatant.

**Table 4.7 NDMA concentration in not ozonated and ozonated centrates entering the primary clarifiers**

Recycle stream	DOC (mg/L)	Ammonia (mg/L as N)	NDMA (ng/L)		
			O <sub>3</sub> /DOC = 0.0	O <sub>3</sub> /DOC = 0.2	O <sub>3</sub> /DOC = 1.0
			mg/mg	mg/mg	mg/mg
Dewatering centrate	269	1250	568	6270	17739
WAST <sup>a</sup> centrate	42	61	50	-	2110

<sup>a</sup> WAST, waste activated sludge thickening.

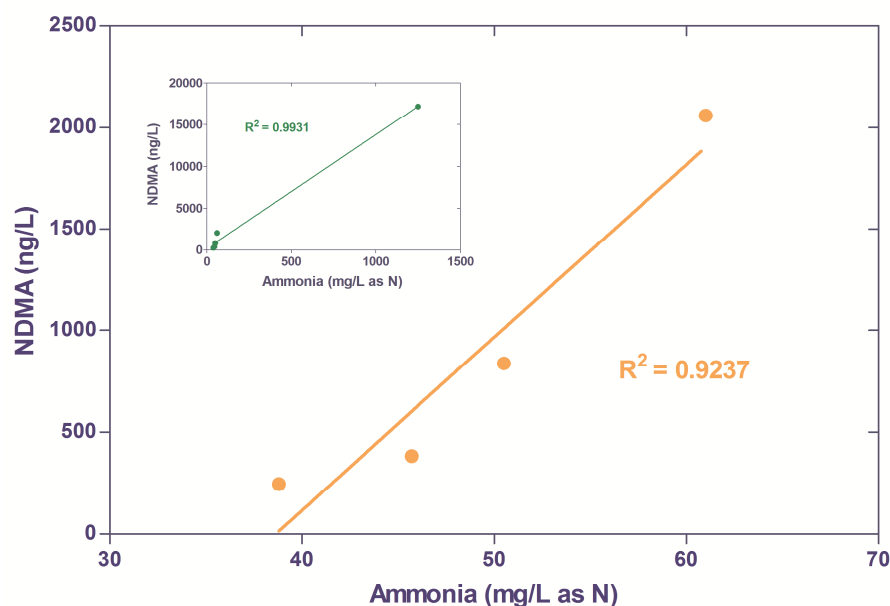
The low amount of NDMA found in the not ozonated WAS centrifuges centrate can be explained again with the significantly lower Mannich polymer dosage.

### 4.3.3 Ammonia and bromide role on NDMA formation

As mentioned in § 2.3.5, Yang et al. (2009) reported two alternative pathways that possibly explain NDMA formation during ozonation at neutral and alkaline pH: (i) secondary amine precursors reacting with HA to form unsymmetrical dimethylhydrazine (UDMH), that is further oxidized to NDMA and (ii) a nitrosation pathway in which dinitrogen tetroxide acts as the nitrosating reagent. HA is a known oxidation byproduct of ammonia and it was shown significantly to increase the NDMA yield from DMA when it was added in DMA containing solutions (Padhye et al., 2011; Andrzejewski et al., 2012). In addition, Padhye et al. (2011) showed that the presence of ozone is critical during reaction of HA with DMA to yield NDMA and that UDMH formed significantly more NDMA when oxidized by ozone than by oxygen. The same study demonstrated that the nitrosation contribution is minimal under neutral and alkaline conditions (Padhye et al., 2011).

The reaction of ammonia (NH<sub>3</sub>) with ozone is very slow with a rate constant of 20.4 M<sup>-1</sup>s<sup>-1</sup>, and pH depended (it seems evident at pH > 7, when free NH<sub>3</sub> is present (negative logarithm of ammonia acid constant dissociation value pK<sub>a</sub><sub>NH<sub>4</sub><sup>+</sup></sub> = 9.25)) (Hoigné and Bader, 1978; Lee and von Gunten, 2010). However, if high level of ammonia concentration is available in water, the ozone-ammonia reaction rate kinetic can be significant. In these conditions, ammonia may be a considerable source of HA increasing the NDMA yields during secondary amines ozonation. In

agreement, good correlation has been found between NDMA formation and ammonia concentration in primary influent, primary effluent, final effluent, and recycle streams ozonated according to  $O_3/DOC$  ratio of 0.9 – 1.0 mg/mg (Figure 4.6).



**Figure 4.6** Correlation between NDMA formation by ozonation ( $O_3/DOC = 0.9 - 1.0$  mg/mg) and ammonia concentration in primary influent, primary effluent, secondary effluent and WAS thickening recycle stream at Hyperion WWTP. Inset shows the correlation including also the data obtained from ozonation of dewatering centrate sample

In order to better investigate the ammonia role on NDMA formation, two known NDMA precursors during chloramination and ozonation, DMA and DMF (Mitch and Sedlack, 2004; Andrzejewski et al, 2008; Oya et al., 2008) were ozonated in DI water with and without ammonia presence. For these experiments, ozone residual was quenched by sodium thiosulfate within 30 seconds. DMA was chosen because it often was used as model precursor for studying NDMA formation pathways (Mitch and Sedlak, 2002b; Choi and Valentine, 2003; Schreiber and Mitch, 2005; Schreiber and Mitch, 2006b; Yang et al., 2009; Padhye et al., 2011), it is a degradation product of Mannich polymer (Park et al.,

2009a) and it was detected in West Basin wastewater influent during a previous study (Mitch and Sedlak, 2004). DMF is a small uncharged molecule with similar ion fragmentation in GC-MS/MS to NDMA and it can be detected by EPA method 521 for NDMA analysis. DMF was detected in the investigated wastewater during the present study.

Because one objective of the study was to investigate NDMA formation mechanisms, solutions of model compounds were prepared at high concentrations. Table 4.8 reports the different conditions of DMA ozonation and the related NDMA formation. Ammonia concentration in DI water and pH were similar to what measured in Hyperion wastewater (Table 3.2). Results confirmed that ammonia presence enhances NDMA formation during ozonation, supporting the hypothesis of increased HA production due to ammonia oxidation. In addition, NDMA formation increased with pH. At higher pH a bigger amount of unprotonated DMA is present in water (negative logarithm of DMA acid constant dissociation value is  $pK_{a_{DMA}} = 10.7$ ) able to react with hydroxylamine to form UDMH; indeed the formation of UDMH is a well-known alkaline catalytic reaction (Mitch and Sedlak, 2002a; Yang et al., 2009). Furthermore, at higher pH, ammonia oxidation is faster (Singer and Zilli, 1975) and thus, a larger amount of free  $NH_3$  can be oxidized to HA by ozone. It was reported that at different pH, ammonia oxidation brings to different concentrations and speciations of end products (i.e. different yield of nitrite and nitrate) (Yang et al., 1999) and probably to different yield of HA.

Experiments also were performed with different ammonia concentrations. Surprisingly, the highest NDMA formation was found at lowest ammonia concentration (20 mg/L as N) and the highest ammonia concentration (100 mg/L as N) lowered the NDMA production. Padhye et al (2011) observed a reduced NDMA formation by ozonation when nitrites were spiked in DMA containing solutions. Likely, elevated nitrites or nitrates production during oxidation of high amount of ammonia may increase the ozone consumption and hinder the NDMA formation via hydroxylamine pathway. Thus, an optimum ratio  $O_3:NH_3$  (pH dependent) can be supposed for enhancing NDMA formation in ammonia and DMA containing water.

NDMA production was also investigated in the presence of bromide ion, which was reported to increase NDMA formation during chloramination and ozonation of several compounds (Padhye et al., 2011; von Gunten et al., 2010; Le Roux et al., 2012). When 4 mg/L of  $Br^-$  were added, the

NDMA formation was almost eight-fold increased, and when bromide ion and ammonia were present concurrently, the NDMA concentration was around fifteen-fold bigger (Table 4.8). Bromide ion ( $\text{Br}^-$ ) improves ammonia oxidation by ozone leading to the production of brominated nitrogen species, such as bromamines (Haag et al., 1984).

**Table 4.8 NDMA formation during ozonation of DMA, ammonia and bromide containing water**

Water Matrix	pH	DMA ( $\mu\text{g/L}$ )	Ammonia ( $\text{mg/L as N}$ )	Bromide ( $\mu\text{g/L}$ )	Ozone ( $\text{mg/L}$ )	NDMA ( $\text{ng/L}$ )
<i>DI water</i>	8	2500	0	0	11	270
<i>DI water</i>	8	2500	50	0	11	320
<i>DI water</i>	8	2500	0	4000	11	2072
<i>DI water</i>	8	2500	50	4000	11	3976
<i>DI water</i>	9	2500	50	0	11	556
<i>DI water</i>	10	2500	50	0	11	715
<i>DI water</i>	8	2500	20	0	11	426
<i>DI water</i>	8	2500	100	0	11	232
<i>Wastewater</i>	-	2500	-	-	11	675
<i>Wastewater</i>	-	0	-	-	11	282
<i>Wastewater</i>	-	0	-	-	0	28

Thus, it seems that when ammonia and bromide are present in water, ozonation of DMA can lead to the formation of NDMA in a similar manner to how proposed when chlorine is added in ammonia and bromide containing water (Chen et al., 2010; Le Roux et al., 2012; Luh and Marinas, 2012).

The NDMA formation pathways reported in Figure 4.7 can be proposed during ozonation of DMA. Similarly to how proposed during chloramination reactions in the presence of bromide (Chen et al., 2010; Le Roux et al., 2012), DMA could react with bromine-containing oxidant species (i.e. bromamines, etc.) to form UDMH or a hypothetical brominated unsymmetrical dimethylhydrazine (UDMH-Br), that subsequently would be oxidized by ozone to NDMA. The bigger amount of NDMA formed can be explained by the improved oxidation of ammonia and DMA in presence of bromide and the subsequent larger formation of brominated oxidants than HA when bromide is absent. Probably, brominated oxidants also have higher reactivity than HA leading to increased amount of UDMH or UDMH-Br.

In addition, when  $\text{Br}^-$  is present, ammonia can be decomposed to gas nitrogen ( $\text{N}_2$ ) by ozonation, and nitrate formation can be decreased, espe-

cially at increased bromide/ammonia ratio (Haag et al., 1984; Yang et al., 1999). This phenomenon can contribute to raise the NDMA yield. Indeed, in this study, nitrites or nitrates presence was supposed to hinder the NDMA formation via hydroxylamine pathway.

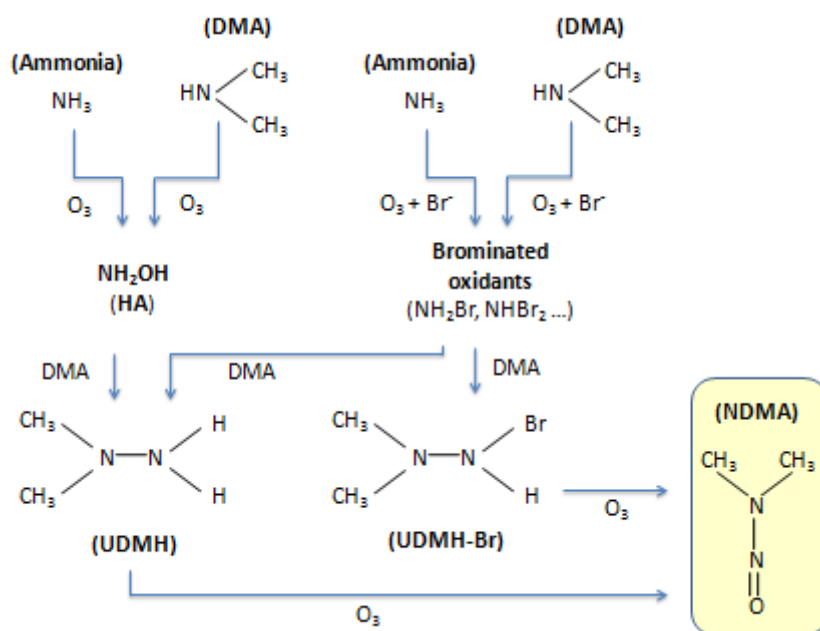


Figure 4.7 Proposed pathways for NDMA formation during ozonation of DMA in the presence of ammonia and bromide

DMA also was spiked in West Basin wastewater influent in order to verify if inorganic water constituents present in this water are able to improve the NDMA yield from DMA. As expected, the net NDMA production in wastewater was around one and a half fold higher than in DI water confirming the important role of inorganic constituents (i.e. ammonia and bromide) even in wastewater matrix.

DMF is an organic compound with dimethylamine functional groups (Figure 4.8). It has a low reactivity with ozone ( $K_{\text{DMF O}_3} = 2.4 \times 10^{-1}$ ) but it is highly reactive with  $\cdot\text{OH}$  radicals ( $K_{\text{DMF } \cdot\text{OH}} = 1.7 \times 10^9$ ) (Lee et al., 2007c). Therefore, DMF may be partially transformed by its reaction with  $\cdot\text{OH}$  radicals during ozonation. In previous studies, during ozonation of DMF, Lee et al. (2007c) observed low yields of DMA (less than 5%) and Oya et al. (2008) found very low yield of NDMA ( $3.5 \times 10^{-4}\%$ ).

In this study, experiments were performed adding TBA or  $\text{H}_2\text{O}_2$  in DI water in order to reduce or increase, respectively, the production of  $\cdot\text{OH}$  radicals during ozonation of DMF. Experiments were repeated in the presence of ammonia. Ozone residual was not quenched in the experiments where ammonia was not added.

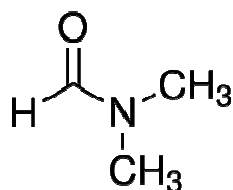


Figure 4.8 Dimethylformamide (DMF) structure

As shown in Table 4.9, no NDMA was detected unless ammonia was present in water and the NDMA formation is attributable to the oxidation of DMF by hydroxyl radicals. In fact, no NDMA was observed when hydroxyl radicals were quenched by addition of TBA. On the other hand, when  $\text{H}_2\text{O}_2$  was added, the NDMA formation increased.

Table 4.9 NDMA formation during ozonation of DMF and ammonia containing water

Water Matrix	pH	DMF ( $\mu\text{g/L}$ )	Ammonia ( $\text{mg/L as N}$ )	TBA (mM)	$\text{H}_2\text{O}_2$ ( $\text{mg/L}$ )	Ozone ( $\text{mg/L}$ )	NDMA ( $\text{ng/L}$ )
DI water	7.6	6600	0	0	0	5.5	ND
DI water	7.6	6600	0	0	5	5.5	ND
DI water	7.6	6600	0	10	0	5.5	ND
DI water	8	2500	50	0	0	11	59
DI water	8	2500	50	0	5	11	101
DI water	8	2500	50	10	0	11	ND
Wastewater	-	2500	-	0	0	11	285
Wastewater	-	2500	-	0	5	11	308
Wastewater	-	0	-	0	0	11	282

ND = not detectable

As previously theorized, ammonia oxidation increases the HA production improving the NDMA yield from the formed DMA. This assumption can explain in part the observed NDMA formation in the presence of ammonia. Likely, other unknown reaction mechanisms may take place.



Spiked DMF in wastewater didn't increase the NDMA formation. Probably, all the produced  $\cdot\text{OH}$  radicals were quenched by effluent organic matter (EfOM). In agreement, when  $\text{H}_2\text{O}_2$  was added in wastewater and the yield of hydroxyl radicals increased, the NDMA formation rose.

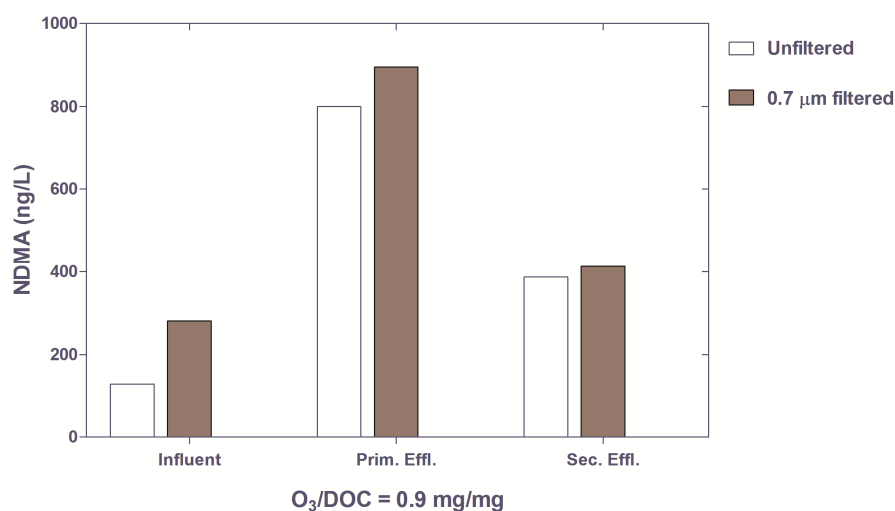
For both the model precursors (DMA and DMF), ammonia presence increased the NDMA yield during ozonation confirming its hypothesized importance on NDMA formation.

#### 4.4 WATER MATRIX EFFECT ON NDMA FORMATION

In this study, primary influent, primary effluent, and secondary effluent of the investigated WWTP were ozonated after  $0.7\ \mu\text{m}$  filtration to explore the NDMA formation within the treatment plant. A prior study reported that the use of DMA-based polyacrylamide (i.e. Mannich) sludge thickening polymers can be a significant source of particle-associated NDMA precursors and a higher NDMA-FP can be present in unfiltered samples compared to  $0.7\ \mu\text{m}$  filtered samples in tests accomplished with high monochloramine dose and extended reaction time (Mitch and Sedlak, 2004). In order to compare the NDMA formation upon ozonation of filtered and unfiltered samples, unfiltered primary influent, primary effluent and secondary effluent of the studied WWTP were ozonated according to the ratio  $\text{O}_3/\text{DOC} = 0.9\ \text{mg/mg}$  and the NDMA formation (Figure 4.9) and UV absorbance spectra (Figure 4.10) were compared to those of the filtered samples.

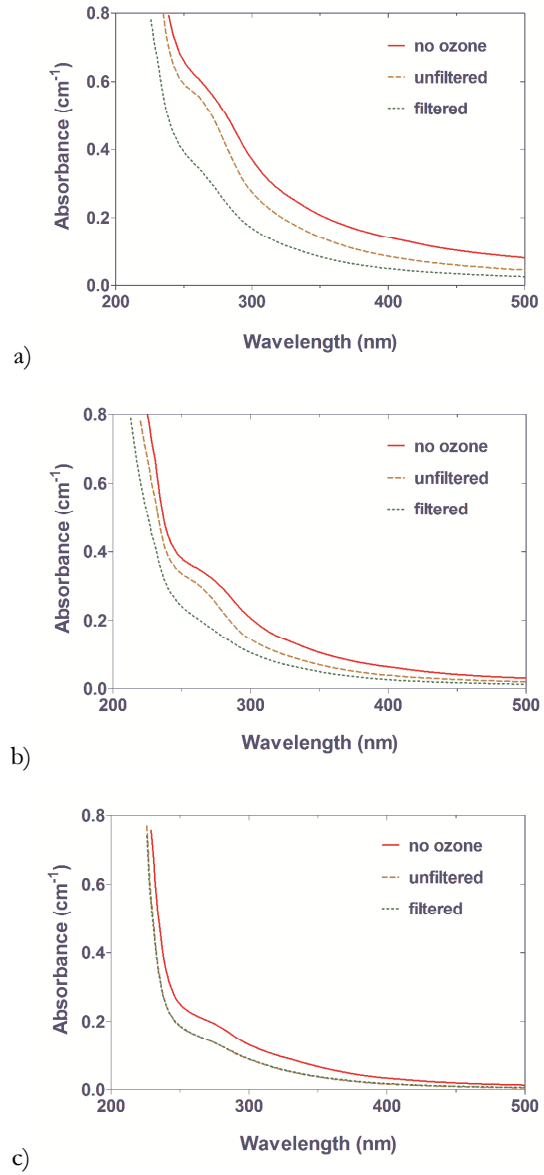
The ozonated filtered sample consistently resulted in higher NDMA concentration as compared to the unfiltered ozonated sample. The biggest difference in NDMA formation between unfiltered and filtered samples was observed for Hyperion WWTP influent (281 ng/L as compared to 130 ng/L). A difference of 95 ng/L was observed for the primary effluent (895 ng/L versus 800 ng/L), whereas the lowest difference was observed for the final effluent (413 ng/L as compared to 387 ng/L). The differences in UV absorbance spectra for ozonated unfiltered and filtered samples reflect the differences in NDMA formation. In particular, the UV spectra of unfiltered and filtered samples from secondary effluent seem exactly overlapped. Likely, filtration lowers ozone demand created by total suspended solids (TSS) allowing more ozone to react

with NDMA precursors. This effect is most dramatic in Hyperion influent samples, which would have the highest levels of TSS. Similarly, TSS hinder the degradation of dissolved chromophores in wastewater organic matter resulting in less decreased UV absorbance.



**Figure 4.9** NDMA formation upon ozonation of 0.7 µm filtered and unfiltered samples. Influent, primary influent; Prim. Effl., primary effluent; Sec. Effl., secondary effluent. Average of triplicate analysis is reported for filtered samples.

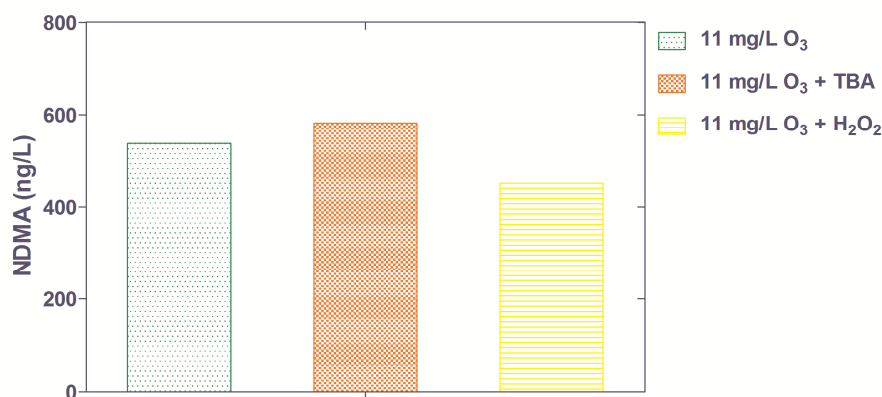
According to these considerations, NDMA formation at the investigated ozonation conditions seems to be mainly related to the reaction between ozone and dissolved precursors in agreement with the hypothesis of polymer degradation and release of dissolved and hydrophilic NDMA precursors. Organic constituents and suspended solids may also affect ammonia oxidation kinetics contributing to explain the obtained results and confirming the ammonia role on NDMA formation.



**Figure 4.10** UV absorbance spectra of a) primary influent, b) primary effluent and c) secondary effluent at Hyperion WWTP. No ozone, no ozonated samples; unfiltered, sample ozonated without previous filtration; filtered, sample ozonated after 0.7  $\mu\text{m}$  filtration. Ozonation was performed according to  $\text{O}_3/\text{DOC} = 0.9 \text{ mg/mg}$

## 4.5 HYDROXYL RADICALS EFFECT ON NDMA FORMATION

Supplementary ozonation experiments were performed adding 5 mg/L of  $\text{H}_2\text{O}_2$  and 10 mM of TBA, a known hydroxyl radical ( $\cdot\text{OH}$ ) scavenger, in Hyperion secondary effluent to investigate a possible role of the hydroxyl radicals on NDMA formation. In fact, previous work has demonstrated that ozone applied to wastewater can rapidly cause decomposition of molecular ozone and the subsequent increased yield of hydroxyl radicals, particularly when the IOD is satisfied or exceeded (Wert et al., 2009). During the current experiments, 11 mg/L of ozone was applied to the investigated wastewater. Figure 4.11 shows that when TBA was added to quench the  $\cdot\text{OH}$  radicals, a slightly increased production of NDMA was observed (582 ng/L as compared to 537 ng/L).



**Figure 4.11** NDMA formation by application of 11 mg/L of ozone ( $\text{O}_3$ ), 11 mg/L of ozone and 10 mM of tert-butyl alcohol (TBA), 11 mg/L of ozone and 5 mg/L of hydrogen peroxide ( $\text{H}_2\text{O}_2$ )

On the other hand, when hydrogen peroxide was added in order to have a higher production of  $\cdot\text{OH}$  radicals the NDMA formation decreased (451 ng/L versus 537 ng/L). This result suggests that  $\cdot\text{OH}$  radicals did not contribute to NDMA formation, but played a role on NDMA destruction due to the higher value of  $\cdot\text{OH}$  rate constant ( $K_{\text{NDMA } \cdot\text{OH}} = 4.6 \times 10^8 \text{ M}^{-1}\text{s}^{-1}$ ) than  $\text{O}_3$  rate constant ( $K_{\text{NDMA } \text{O}_3} = 5.3 \times 10^{-2} \text{ M}^{-1}\text{s}^{-1}$ ) for NDMA (Lee et al., 2007b). Probably, the yield of hydroxyl radicals was quickly quenched by effluent organic matter (EfOM) and other water

constituents and it was not enough to induce degradation of more complex NDMA precursors as previously shown in other works (Padhye et al., 2011).

#### 4.6 USE OF SPECTROSCOPIC MEASUREMENTS TO CONTROL NDMA FORMATION DURING OZONATION

Pre-ozonated samples collected at the pilot system at West Basin WWRP were further ozonated with ozone doses of 3.5, 7, 11, 14 and 18 mg/L. NDMA analyses and spectroscopic measurements (UV absorbance and fluorescence) were accomplished for all the samples. As shown in Figure 4.12, NDMA formation increased with the increased ozone dose up to an ozone dose of 11 mg/L. After that a plateau was evident due to the consumption of all the precursors, and the NDMA concentration started to decrease slightly, probably because of the increased yield of hydroxyl radicals at higher ozone dose (Wert et al., 2009); indeed, the NDMA oxidation is known to be dominated by  $\cdot\text{OH}$  radicals (Lv et al., 2013).

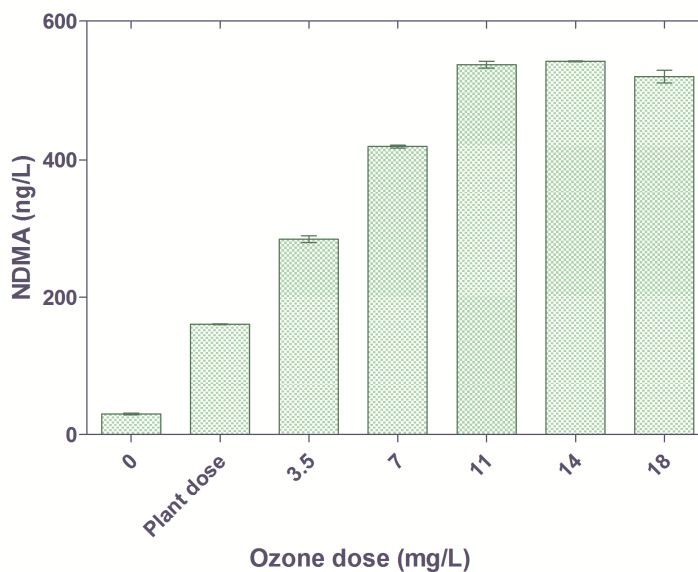
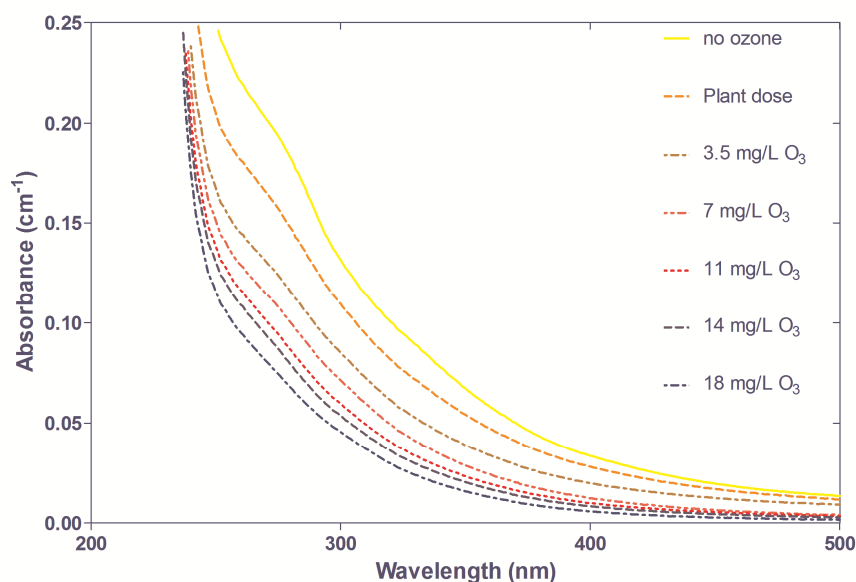


Figure 4.12 NDMA formation in West Basin WWRP influent at different ozone doses. Plant dose, pre-ozonated samples

Figure 4.13 and Figure 4.14 show, respectively, the decreased UV absorbance and fluorescence with the increased ozone dose due to the degradation of chromophores in effluent organic matter (EfOM). Figure 4.15 reports correlations between NDMA formation and UV absorbance removal at 272 nm ( $UV_{272\text{ rem}}$ ), and between NDMA formation and total fluorescence removal ( $\Phi_{T\text{ rem}}$ ). These correlations are related to samples ozonated with doses up to 11 mg/L, id est only when NDMA formation occurred.



**Figure 4.13** UV absorbance spectra of West Basin wastewater influent at different ozone doses. Plant dose, pre-ozonated samples

Similar correlations were observed for all the other tested wastewaters in this study (i.e. Roger Road, Ina Road and Green Valley final As shown in

Table 4.10, always a linear regression with a square correlation factor ( $R^2$ ) higher than 0.8 occurred. The regression slope was different for different waters, and it was higher in wastewater with more elevated concentration of NDMA precursors (i.e. water with higher NDMA formation) and higher values of total nitrogen (TN) and DOC. It suggests that extended biological treatment and biological nitrogen removal reduce the load of NDMA precursors in wastewater.

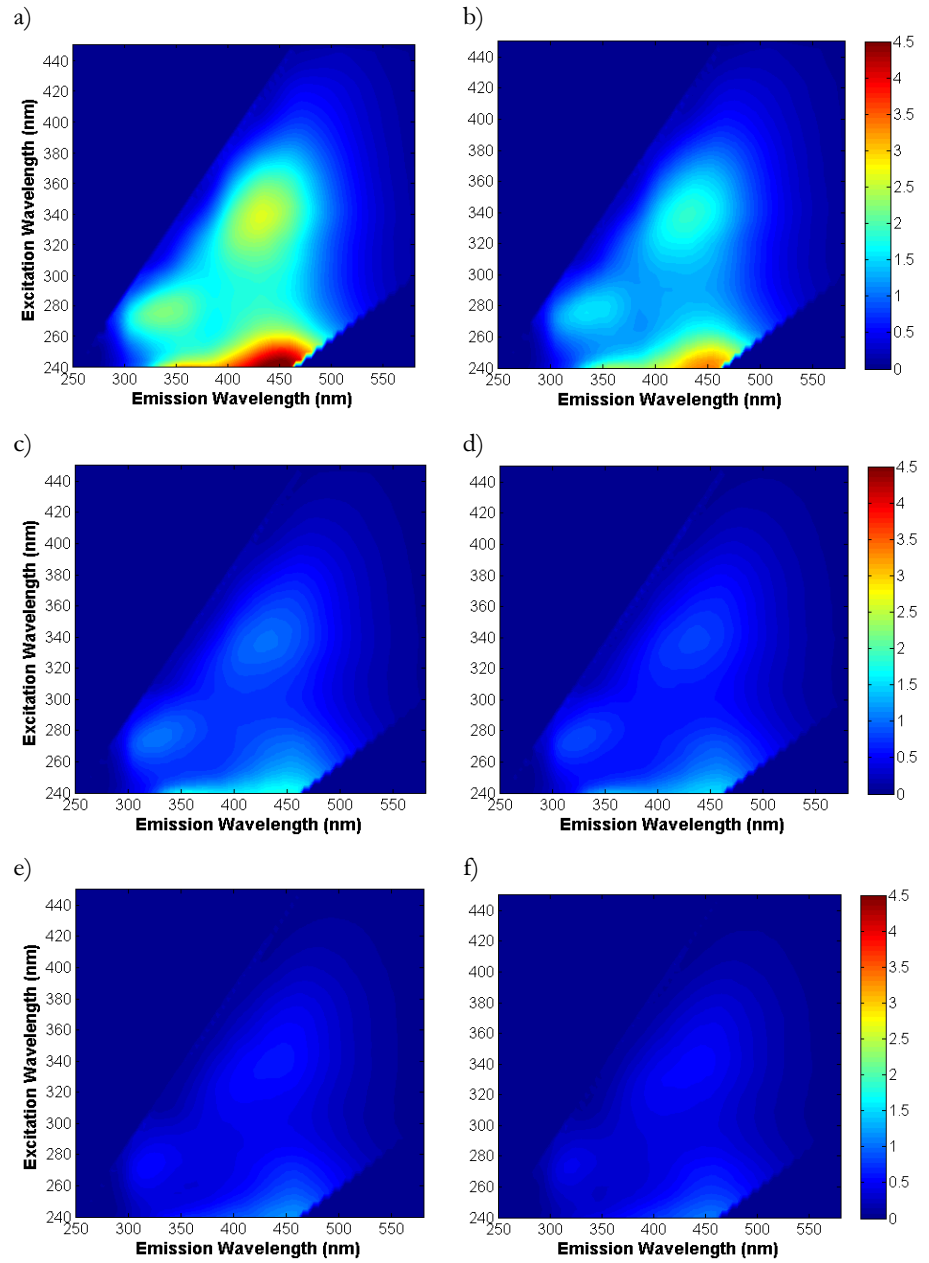
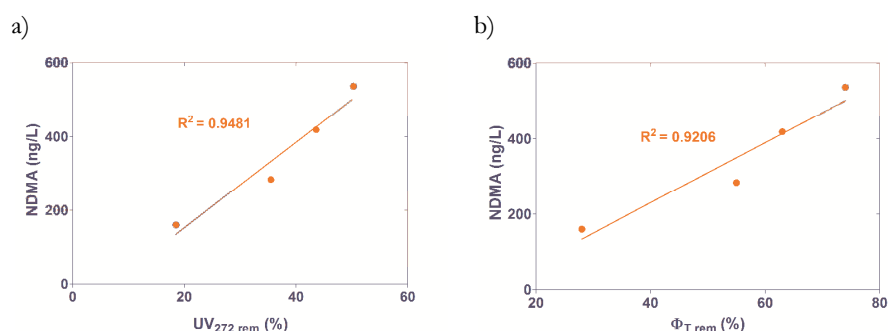


Figure 4.14 EEMs of West Basinn influent a) not ozonated, and ozonated with b) plant dose and c) 3.5 mg/L, d) 7 mg/L, e) 11 mg/L, f) 14 mg/L

**Table 4.10** Max NDMA formation in different wastewaters and regression parameters of correlations between NDMA formation and UV absorbance at 272 nm ( $UV_{272}$ ) removal, and NDMA formation and total fluorescence ( $\Phi_T$ ) removal

Wastewater effluent	NDMA <sub>max</sub> (ng/L)	$UV_{272}$ slope	$\Phi_T$ slope	$R^2_{UV}$	$R^2_{\Phi_T}$
Hyperion	512	11.6	8.0	0.95	0.92
Roger road	29	0.9	0.6	0.99	0.99
Ina Road	5	0.1	0.1	0.98	0.97
Green Valley	4	0.1	0.1	0.95	0.84



**Figure 4.15** Correlation between NDMA formation and a)  $UV_{272}$  absorbance removal ( $UV_{272\text{ rem}}$ ), b) total fluorescence removal ( $\Phi_{T\text{ rem}}$ )

Hence, in all the studied wastewaters the degradation of chromophores in EfOM by ozonation seems to be well correlated to the oxidation of NDMA precursors and to the consequent NDMA formation. Similar observation was reported in § 4.4, where the water matrix effect on NDMA formation was investigated.

## 4.7 ULTRAVIOLET TREATMENT OF DMF

DMF belong with dimethylamides group, in which dimethylamine functional groups are adjacent to electron-withdrawing thionyl or carbonyl functional groups. During chloramination, dimethylamides are relatively unreactive because the electron-withdrawing thionyl or carbonyl groups renders the adjacent dimethylamine functional groups unreactive to elec-



trophilic attack by chloramines and the potential NDMA formation is attributable to release of DMA (Mitch and Sedlak, 2004).

DMF is a small uncharged molecule able to pass RO membranes to a larger extent. Particularly, DMF was detected in RO permeate at West Basin WWRP, and an enhanced NDMA formation during the final chlorination has been observed when hydrogen peroxide was fed to the UV system (Figure 4.1). Thus, it was hypothesized that UV or UV/H<sub>2</sub>O<sub>2</sub> treatment of DMF may form more reactive NDMA precursors (i.e. DMA) and enhance the NDMA formation during a post chloramination. To verify this hypothesis, bench scale ultraviolet experiments described in § 3.3.2 were performed by LPUV collimated beam device.

As shown in Table 4.11, NDMA formation increased during photolysis in the presence of H<sub>2</sub>O<sub>2</sub>.

**Table 4.11 NDMA formation during chloramination after UV and UV/H<sub>2</sub>O<sub>2</sub> treatment of DMF**

<b>Water Matrix</b>	<b>pH</b>	<b>DMF (µg/L)</b>	<b>Ammonia (mg/L as N)</b>	<b>H<sub>2</sub>O<sub>2</sub> (mg/L)</b>	<b>UV dose (mJ/cm<sup>2</sup>)</b>	<b>Cl<sub>2</sub> (mg/L)</b>	<b>NDMA (ng/L)</b>
<i>DI water</i>	8	2500	4	0	0	4	10
<i>DI water</i>	8	2500	4	0	250	4	4
<i>DI water</i>	8	2500	4	0	500	4	6
<i>DI water</i>	8	2500	4	0	1000	4	10
<i>DI water</i>	8	2500	4	3	250	4	49
<i>DI water</i>	8	2500	4	3	500	4	128
<i>DI water</i>	8	2500	4	3	1000	4	195

UV/H<sub>2</sub>O<sub>2</sub> treatment is known to produce hydroxyl radicals in water, oxidant specie highly reactive with DMF (Lee et al., 2007c). As reported in § 4.3.3 for ozonation experiments, ·OH radicals oxidize DMF leading to the release of DMA (Lee et al., 2007c). Thus, an enhanced NDMA formation may come from the formed DMA after UV/H<sub>2</sub>O<sub>2</sub> oxidation of DMF. The increased NDMA formation with the increased UV dose in the presence of H<sub>2</sub>O<sub>2</sub>, can be explained by the improved yield of ·OH radicals, that oxidize more DMF to DMA.



## 5 CONCLUSIONS

Scientists have been studying nitrosamines for more than 100 years. However, nitrosamines gained more attention after 1954, when the carcinogenic properties of the group were discovered (Barnes and Magee, 1954). It has been proved that roughly 90% of nitrosamines are carcinogenic, but NDMA is the subject of the majority of studies in literature. It has been the nitrosamine most commonly detected in drinking water and wastewater (USEPA, 2012). As a polar compound, NDMA is not bioaccumulated, but also appears to be hardly biodegradable. The large hydrophilicity, the low adsorbability and the recalcitrant nature of nitrosamines contribute to a large risk of ground water contamination. However, the most serious threat for consumers results from the generation of NDMA during final disinfection of drinking water, issue noticed worldwide and especially in wastewater impaired potable supply.

This study handles the formation and control of NDMA in wastewater treatments employing advanced processes, including ozonation, RO, photolysis, and AOPs (i.e. UV/H<sub>2</sub>O<sub>2</sub>) and aimed at indirect potable reuse. Based on the data obtained in this study, the following conclusions can be presented:

- ✓ RO is confirmed to remove the vast majority of NDMA precursors, but to not be an efficient technology in NDMA rejection.
- ✓ H<sub>2</sub>O<sub>2</sub> hinders NDMA photolysis due to the absorption/screening of UV light, which lowers the number of photons reaching NDMA molecules. However, this effect depends on UV dose and H<sub>2</sub>O<sub>2</sub> concentration.
- ✓ Different UV doses and the H<sub>2</sub>O<sub>2</sub> presence in photolysis treatment affect the NDMA (re)formation during post chloramination. Particularly, lower UV doses and treatment with H<sub>2</sub>O<sub>2</sub> were observed to enhance the NDMA formation. Probably, the formed by-products have higher NDMA formation rate compared to the parent compounds during chloramination. On the other hand, extended oxidations and high UV

doses reduced the final NDMA (re)formation, likely, due to the further oxidation of the more reactive by-products. In any case, depending on UV dose, precursors and  $\text{H}_2\text{O}_2$  concentration, the NDMA (re)formation by chloramination after UV/ $\text{H}_2\text{O}_2$  treatment may produce values not in compliance with water reuse requirements.

- ✓ In this study, UV/ $\text{H}_2\text{O}_2$  treatment of DMF (NDMA precursors detected in the investigated water matrix) was proved to enhance the NDMA formation during post chloramination. DMF is highly reactive with hydroxyl radicals and its oxidation releases the known NDMA precursor DMA.
- ✓ Often, ozonation of wastewaters leads to the rapid formation of NDMA levels not in compliance with potable reuse requirements. In this study, it was observed in wastewater of different characteristics. Furthermore, NDMA formation depends on the applied ozone doses due to the high IOD common for wastewaters and the quick depletion of ozone.
- ✓ In water with elevated load of NDMA precursors, very high and rapid NDMA formation by ozone may occur, whereas the much slower chloramination kinetics produce far lower amount of NDMA at dosage and contact time typical of wastewater reclamation plant.
- ✓ Finally, in the investigated wastewater in this study, post-chloramination after ozonation at different ozone doses resulted always in a same slight rise of NDMA at brief reaction time ( $\sim 3$  hours). In addition, pH adjustment (from pH 5.6 to pH 8) increased the NDMA formation during chloramination even in pre-ozonated wastewater.

Different ozonation tests were performed using wastewater collected at Hyperion WWTP (Los Angeles, California (USA)) in order to figure out the source of NDMA precursors in this wastewater characterized by unusual extremely high NDMA formation during ozonation. Ozone doses normalized to DOC concentration and applied to the primary influent, primary effluent, and secondary effluent of the treatment plant showed the most NDMA production in the primary effluent, and the recycle streams entering the primary clarifier were identified as the main source of NDMA precursors. The degradation of aminomethylated polyacrylamide (Mannich) polymer used for sludge treatment and the following re-

lease of dissolved compounds (e.g. dimethylamine) was the principal cause of precursors' occurrence.

An important role of the inorganic water constituents ammonia and bromide on NDMA formation by ozonation was demonstrated in this work. Ozonation of ammonia and bromide in water leads to the formation of HA and brominated oxidants (e.g. bromamines) that are able to improve the NDMA yield from some precursors, including DMA and DMF. Thus, new NDMA formation pathways during ozonation were proposed using DMA as model precursors and including the role of ammonia and bromide. Ozonation of ammonia and secondary amines forms HA; ozonation of ammonia and secondary amines in the presence of bromide forms brominated oxidants (i.e. bromamines, etc.). DMA reacts with HA to form UDMH, which subsequently is oxidized by ozone to NDMA. Similarly, when bromide is present in water, DMA reacts with bromine-containing oxidant species to form UDMH or a hypothetical UDMH-Br, which subsequently is oxidized by ozone to NDMA. The higher amount of NDMA formed when bromide is present can be explained by the improved oxidation of ammonia and secondary amines and the subsequent larger formation of brominated oxidants than HA when bromide is absent. Furthermore, an optimum ratio  $O_3:NH_3$  (pH dependent) seems to maximize the NDMA formation in ammonia and DMA containing water. The reason is not clear and likely related to yield of nitrite or nitrate during ammonia oxidation.

Ammonia role on NDMA formation was also confirmed during ozonation of DMF containing solution. Indeed NDMA was detected only when ammonia was present in water and the NDMA formation was attributable to the oxidation of DMF by hydroxyl radicals. In agreement, it was reported that DMF is highly reactive with  $\cdot OH$  radical, whereas it has very low reactivity with ozone (Lee et al., 2007c).

During ozonation of Hyperion wastewater, filtered samples (0.7  $\mu m$ ) produced more NDMA than unfiltered samples suggesting that only dissolved compounds reacted with ozone to form NDMA. Likely, filtration lowered ozone demand created by TSS allowing more ozone to react with NDMA precursors. Finally, it was found that during ozonation of Hyperion effluent,  $\cdot OH$  radicals had no additional contribution to NDMA formation but actually played a role of NDMA destruction. In agreement, DMF was not the main precursor of this water and its presence was not significant.

Linear correlation between NDMA formation during ozonation and UV absorbance removal at 272 nm and total fluorescence removal were observed for different wastewater matrices. It suggests that in wastewaters, the degradation of chromophores in EfOM by ozonation is well correlated to the oxidation of NDMA precursors.

Results of this study offer important guidance for strategies to minimize the potential of NDMA formation in wastewater destined for indirect potable reuse and may help to better address future research on NDMA source control.

Ozonation of wastewater characterized by elevated ammonia and NDMA precursors' occurrence can induce high and rapid NDMA formation. For example, in Hyperion wastewater effluent, the application of an oxidant other than ozone may be preferable since chloramination resulted in far lower amounts of NDMA. In any case, the most appropriate strategy will depend on specific plant configuration, water quality, and planned uses of the resulting water.

RO followed by UV/H<sub>2</sub>O<sub>2</sub> is the gold technology to control and remove NDMA during water reuse applications. NDMA is not rejected by RO membrane and elevated NDMA concentrations will need high energy consumption in a following UV treatment for a substantial photo-degradation.

Depending on water quality and NDMA precursors concentration, UV/H<sub>2</sub>O<sub>2</sub> treatment may also enhance NDMA formation during a post chloramination. Thus, the designed UV dose should be validated not only in terms of NDMA removal but the design parameters should take account the potential NDMA (re)formation during post-chloramination. In addition, the use of H<sub>2</sub>O<sub>2</sub> may need to be avoided.

The use of DMA-based polyacrylamide polymers (i.e. Mannich polymer) in sludge thickening and dewatering should be avoided in wastewater treatment plant due to their easily degradable structure that can release elevated amount of dissolved NDMA precursors in the centrates sent back to the head of the treatment plant becoming an important NDMA precursors source in wastewater.

The absence of ammonia reduces hydroxylamine formation (or bromine-containing nitrogen oxidants formation, if bromide is present) during ozonation and NDMA yields of amines and amides will then be significantly lower. Therefore, a complete biological nitrification may represent an effective treatment method for reducing NDMA formation potential.

Furthermore, biological treatment for nitrogen removal of supernatants would significantly reduce the ammonia load in the main stream of a wastewater treatment plant and may help to degrade NDMA precursors released during the previous sludge treatments (Fux et al., 2002).

This is the first study to identify the main cause of NDMA formation by ozonation within a full scale wastewater treatment plant, including the sludge treatment train, indicating that further research is needed to better evaluate the role of biological processes to degrade complex molecules and release potential NDMA precursors. More studies into the occurrence and control of inorganic nitrogenous substances, such as nitrite, nitrate, ammonia, and hydroxylamine are also needed.





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