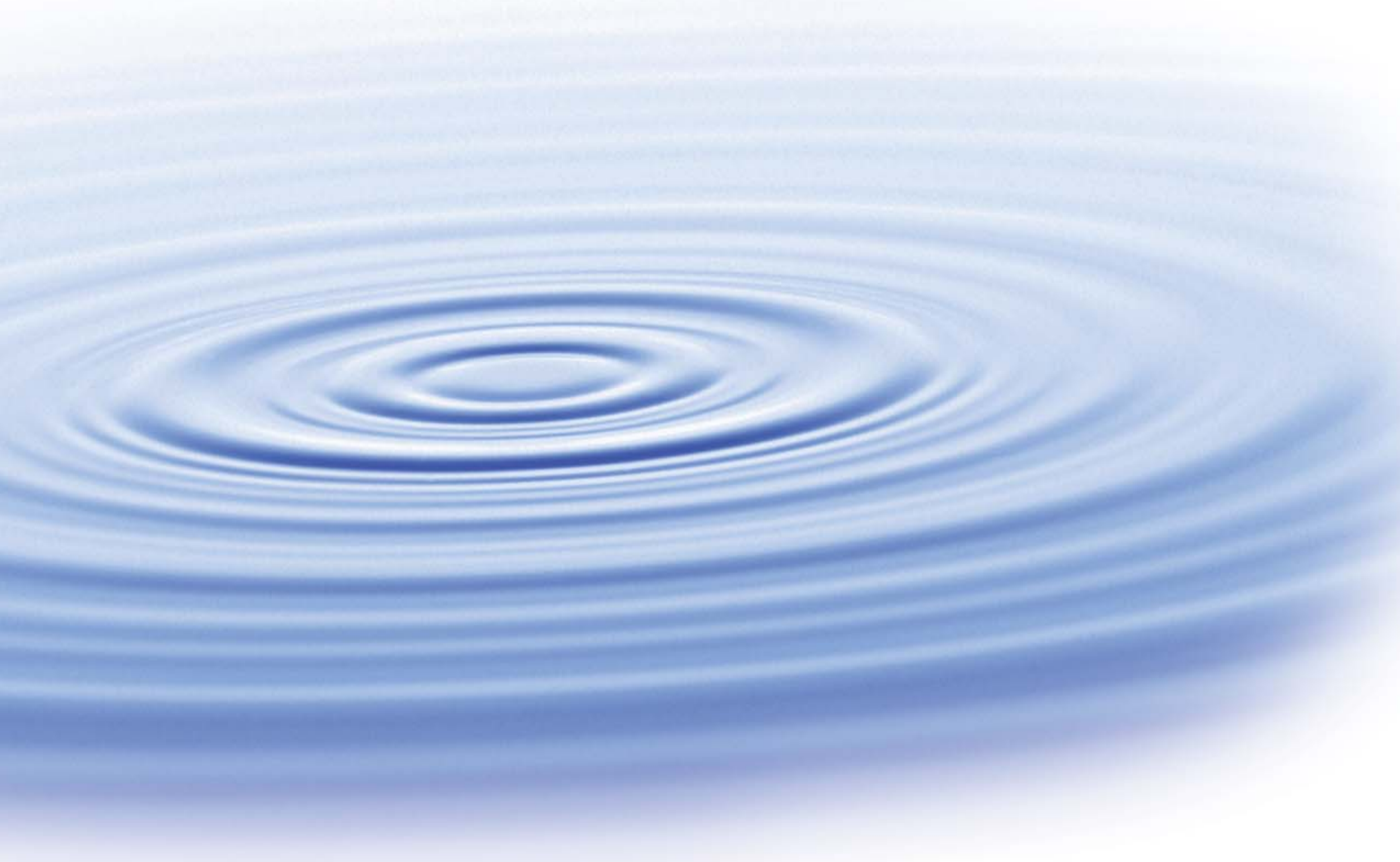
WATEREUSE
FOUNDATION

Removal and Destruction of NDMA and NDMA Precursors during Wastewater Treatment



WateReuse
Foundation

Removal and Destruction of NDMA and NDMA Precursors during Wastewater Treatment

About the WateReuse Foundation

The mission of the WateReuse Foundation is to conduct and promote applied research on the reclamation, recycling, reuse, and desalination of water. The Foundation's research advances the science of water reuse and supports communities across the United States and abroad in their efforts to create new sources of high quality water through reclamation, recycling, reuse, and desalination while protecting public health and the environment.

The Foundation sponsors research on all aspects of water reuse, including emerging chemical contaminants, microbiological agents, treatment technologies, salinity management and desalination, public perception and acceptance, economics, and marketing. The Foundation's research informs the public of the safety of reclaimed water and provides water professionals with the tools and knowledge to meet their commitment of increasing reliability and quality.

The Foundation's funding partners include the U.S. Bureau of Reclamation, the California State Water Resources Control Board, the Southwest Florida Water Management District, and the California Department of Water Resources. Funding is also provided by the Foundation's Subscribers, water and wastewater agencies, and other interested organizations. The Foundation also conducts research in cooperation with two water research coalitions – the Global Water Research Coalition and the Joint Water Reuse & Desalination Task Force.

Removal and Destruction of NDMA and NDMA Precursors during Wastewater Treatment

Principal Investigators
David Sedlak, Ph.D.
University of California, Berkeley

Michael Kavanaugh, Ph.D., P.E., DEE
Malcolm Pirnie, Inc.

Project Team
City of San Jose, California
City of Scottsdale, Arizona
Sanitation Districts of Los Angeles County
Orange County Water District
Orange County Sanitation District
West Basin Municipal Water District
Malcolm Pirnie, Inc.
McGuire Environmental Consultants, Inc.

Published by the WateReuse Foundation
Alexandria, VA

Disclaimer

For more information, contact:
WateReuse Foundation
1199 North Fairfax Street, Suite 410
Alexandria, VA 22314
703-548-0880
703-548-5085 (fax)
www.WateReuse.org/Foundation

WateReuse Foundation Project Number: WRF-01-002
WateReuse Foundation Product Number: 01-002-01

ISBN: 0-9747586-8-X
Library of Congress Control Number: 2005937963

Printed in the United States of America

CONTENTS

FIGURES

TABLES

FOREWORD

The WateReuse Foundation, a nonprofit corporation, sponsors research that advances the science of water reclamation, recycling, reuse, and desalination. The Foundation funds projects that meet the water reuse and desalination research needs of water and wastewater agencies and the public. The goal of the Foundation's research is to ensure that water reuse and desalination projects provide high-quality water, protect public health, and improve the environment.

A Research Plan guides the Foundation's research program. Under the plan, a research agenda of high-priority topics is maintained. The agenda is developed in cooperation with the water reuse and desalination communities, including water professionals, academics, and Foundation Subscribers. The Foundation's research focuses on a broad range of water reuse research topics including the following:

- Defining and addressing emerging contaminants;
- Public perceptions of the benefits and risks of water reuse;
- Management practices related to indirect potable reuse;
- Groundwater recharge and aquifer storage and recovery;
- Evaluating methods for managing salinity and desalination; and
- Economics and marketing of water reuse.

The Research Plan outlines the role of the Foundation's Research Advisory Committee (RAC), Project Advisory Committees (PACs), and Foundation staff. The RAC sets priorities, recommends projects for funding, and provides advice and recommendations on the Foundation's research agenda and other related efforts. PACs are convened for each project and provide technical review and oversight. The Foundation's RAC and PACs consist of experts in their fields and provide the Foundation with an independent review, which ensures the credibility of the Foundation's research results. The Foundation's Project Managers facilitate the efforts of the RAC and PACs and provide overall management of projects.

The Foundation's primary funding partners are the U.S. Bureau of Reclamation, the California State Water Resources Control Board, the Southwest Florida Water Management District, the California Department of Water Resources, Foundation Subscribers, water and wastewater agencies, and other interested organizations. The Foundation leverages its financial and intellectual capital through these partnerships and funding relationships. The Foundation is also a member of two water research coalitions: the Global Water Research Coalition and the Joint Water Reuse & Desalination Task Force.

This publication is the result of a Foundation-sponsored study and is intended to communicate the results of this research project. The goals of this project were to develop an understanding of the fate of NDMA precursors and NDMA during conventional treatment processes and to select and validate a model to predict its destruction using UV technology.

Ronald E. Young
President
WateReuse Foundation

G. Wade Miller
Executive Director
WateReuse Foundation

ACKNOWLEDGMENTS

This study would not have been possible without the dedication of the following individuals and organizations: Ed Means, P.E., and Michael McGuire, P.E. (Malcolm Pirnie, Inc., formerly McGuire Environmental Consultants, Inc.); Lucia McGovern (Camarillo Sanitary District, formerly at West Basin Municipal Water District); Jennifer Bender and Richard Nagel (West Basin Municipal Water District); Rodger Baird (Sanitation Districts of Los Angeles County); Chris Baker, Chris Berch, and Doug Drury (Inland Empire Utilities District); David Tucker, Eric Hansen, Eric Rosenblum, and Jessie E. Denver (City of San Jose, California); Jim Clune (City of Scottsdale, Arizona); Karin North (City of Palo Alto, California); John Hayes (Irvine Ranch Water District); Kim Christensen (Orange County Sanitation District).

The project team would like to thank the WateReuse Foundation for funding this applied research project, as well as the following organizations for their in-kind contributions: West Basin Municipal Water District, Sanitation Districts of Los Angeles County, Orange County Sanitation District, Orange County Water District, City of Scottsdale, Arizona, and Malcolm Pirnie, Inc.

Principal Investigators

David Sedlak, Ph.D., *University of California, Berkeley*
Michael C. Kavanaugh, Ph.D., P.E., DEE, *Malcolm Pirnie, Inc.*

Project Manager

Rula A. Deeb, Ph.D., *Malcolm Pirnie, Inc.*

Project Team

Steve Carr, *Sanitation Districts of Los Angeles County*
Zaid K. Chowdhury, Ph.D., P.E., *Malcolm Pirnie, Inc.*
Uzi Daniel, *West Basin Municipal Water District*
Joanne Daugherty, *Orange County Water District*
Tim Durbin, *University of California, Berkeley*
James Ervin, *City of San Jose, California*
Steve Fitzsimmons, *Orange County Water District*
Elisabeth L. Hawley, P.E., *Malcolm Pirnie, Inc.*
Jon Loveland, Ph.D., *Malcolm Pirnie, Inc. (formerly of McGuire Environmental Consultants)*
William Mitch, Ph.D., *Yale University (formerly of University of California, Berkeley)*
Sam Mowbray, Ph.D., *Orange County Sanitation District*
Gregg Oelker, *United Water*
Elif Pehlivanoglu, Ph.D., *Istanbul Technical University (formerly of University of California, Berkeley)*
Hannah Truong, *City of San Jose, California*
William Vernon, *City of Scottsdale, Arizona*
Michael Wehner, *Orange County Water District*

Project Advisory Committee

Harold Bailey, Ph.D., *Padre Dam Municipal Water District*
Joseph Cotruvo, Ph.D., *Joseph Cotruvo & Associates*
Andy Murphy, *U.S. Bureau of Reclamation*
Diana Messina, *California State Water Resources Control Board*
Andrew Salveson, P.E., *Carollo Engineers*

EXECUTIVE SUMMARY

PROJECT BACKGROUND AND OBJECTIVES

The WateReuse Foundation identified a need for research to investigate the removal and/or destruction of *N*-nitrosodimethylamine (NDMA) and NDMA precursors during wastewater treatment processes. NDMA is a probable human carcinogen with health concerns at very low concentrations. The State of California Department of Health Services (CalDHS) established a drinking water notification level of 10 ng/L of NDMA in 2002. In response to growing scrutiny of NDMA impacts, wastewater utilities that are practicing water reuse may need to evaluate NDMA sources, formation, removal, and advanced treatment processes specific to NDMA in order to reliably and cost-effectively reduce concentrations in the final product water.

Funded by the WateReuse Foundation, Malcolm Pirnie, in association with the University of California at Berkeley (UC Berkeley), managed a three-year applied research project to investigate the formation and removal of NDMA and NDMA precursors during wastewater treatment at facilities where indirect potable reuse is practiced. Co-principal investigators were Dr. Michael Kavanaugh from Malcolm Pirnie and Dr. David Sedlak from UC Berkeley. The project team also included representatives from Orange County Water District (OCWD), Orange County Sanitation District (OCSD), Sanitation Districts of Los Angeles County (LACSD), West Basin Municipal Water District (WBMWD), the City of San Jose, California, the City of Scottsdale, Arizona, and McGuire/Malcolm Pirnie (formerly McGuire Environmental Consultants, Inc.).

The project objectives were as follows:

- To assess the importance of industrial sources of NDMA and NDMA precursors entering wastewater treatment plants.
- To understand the fate of NDMA precursors and NDMA during conventional treatment processes.
- To understand NDMA formation during conventional and advanced treatment.
- To select and validate a model to predict NDMA destruction using UV technology.
- To communicate research results to water utility personnel and other environmental professionals.

Specifically, the research was organized into six key tasks:

Task 1: Conduct a workshop to assess the state of the art on NDMA sources, fate, and control;
Task 2: Assess the importance of industrial sources of NDMA and NDMA precursors;
Task 3: Assess the removal of NDMA and NDMA precursors in conventional wastewater treatment plants;
Task 4: Assess the removal of NDMA and NDMA precursors in advanced wastewater treatment plants;
Task 5: Develop and validate a model for the efficacy of UV treatment systems for NDMA; and
Task 6: Project reporting and outreach.

PROJECT APPROACH

As part of Task 1, the project team held a workshop at the beginning of the project to summarize the quickly evolving state of knowledge regarding NDMA. Project team members and invited workshop participants discussed their experiences and ongoing projects related to NDMA, including monitoring programs, analytical techniques, NDMA precursors, industrial sources, formation, removal and destruction of NDMA, and data gaps. The remainder of the workshop was used to refine the project approach, objectives, and sampling plan.

Information from the workshop was incorporated into the scope of work for Tasks 2 through 4. Task 2 involved collecting samples from the influent of seven different wastewater treatment facilities with a range of industrial discharges within the collection area (ranging from <2% to 18% by volume) to assess the importance of industrial sources of NDMA and NDMA precursors to wastewater treatment plants. Wastewater samples were collected from trunklines and industrial wastewater discharges to quantify NDMA and NDMA precursor concentrations resulting from specific industrial practices. For Task 3, the project team collected primary and secondary effluent samples from seven different facilities to investigate the fate of NDMA and NDMA precursors during conventional air activated sludge wastewater treatment. As part of Task 4, samples were collected from three different utilities to document the typical profile of NDMA and NDMA precursors during advanced treatment [microfiltration (MF), reverse osmosis (RO), and UV treatment]. Laboratory-scale and pilot-scale studies were conducted at one facility to examine the benefits of preforming monochloramines before adding them to wastewater, as well as the effect of pH on NDMA formation. Task 5 consisted of developing and validating a water quality-based photolysis model that could be used to predict NDMA removal during UV treatment and/or advanced oxidation (e.g., UV and hydrogen peroxide). The model can be used to predict how much electricity is needed to achieve the desired percent NDMA removal as a function of influent water quality, reactor configuration, and lamp type. Model predictions were compared with empirical results from a pilot-scale UV treatment system tested at OCWD. The effect of advanced oxidation on NDMA was also modeled, using a steady-state hydroxyl radical approximation. Finally, Task 6 was accomplished by communicating results in periodic progress reports and through professional outreach activities (e.g., conference presentations, peer-reviewed journal publications).

The original project scope was amended to include a Project Addendum to investigate NDMA occurrence and formation in nonpotable water reuse systems. Wastewater utilities may need to address NDMA in nonpotable water reuse systems due to the potential for NDMA formed in such systems to enter potable water supplies. Samples were collected at six different facilities practicing nonpotable reuse. Laboratory studies were performed to quantify the relationship between chlorine dose, NDMA precursor concentration, and NDMA formation.

PROJECT FINDINGS

During the workshop, some of the key aspects of NDMA were discussed. NDMA is an industrial contaminant that can be present in lubricants, copolymers, antifreeze, and rubber. The compound is also a breakdown product of the rocket fuel component unsymmetric dimethylhydrazine (UDMH). Past industrial operations are responsible for NDMA detected in groundwater at California sites such as San Gabriel Valley and the Aerojet facility in Rancho Cordova. NDMA has been detected in the influent to wastewater treatment plants such as OCSD at average daily concentrations greater than 400 ng/L.

NDMA has also been shown to form as a disinfection byproduct, particularly in water that is high in organic material, such as treated wastewater. NDMA is particularly a concern for utilities that practice indirect potable reuse using chlorinated treated wastewater effluents. The compound is highly soluble (100 g/L at 20°C) and may persist in aquifers following reinjection of tertiary treated wastewater. NDMA detections of 30–40 ng/L in Orange County drinking water wells near a groundwater recharge zone led to temporary well closure in 2002. In California, the notification level for NDMA and its status as a U.S. Environmental Protection Agency priority toxic pollutant have led to the inclusion of monitoring requirements for NDMA in the draft Title 22 Recharge and Reuse Requirements, which are applicable to all utilities practicing indirect potable reuse in the state of California. In preparation for future regulations, some utilities have installed UV treatment units to remove NDMA.

There is currently no regulatory-approved method for measuring NDMA at low levels in drinking water. At this time, CalDHS has no plans to develop a standard analytical method for NDMA but is evaluating data acceptability and certifying laboratories on a case-by-case basis. The most common analytical method for NDMA consists of liquid-liquid extraction, evapoconcentration, gas chromatography, and mass spectroscopy followed by low-resolution chemical ionization or high-resolution electron impact mass spectroscopy. Solid-phase extraction techniques using disks or cartridges of absorbent material such as Ambersorb are also commonly used for NDMA. The reportable detection limit for NDMA is approximately 2 ng/L in samples with relatively low concentrations of organic material. NDMA analyses are not widely available at commercial laboratories, and the cost per sample is high (up to $370 per sample), despite research to develop cheaper yet reliable analytical methods. A research project sponsored by the WateReuse Foundation titled *Alternative Methods for the Analysis of NDMA and Other Nitrosamines in Water and Wastewater* (WRF-01-001) was conducted concurrently with this project to summarize the latest advances in analytical methods for nitrosamines.

During water or wastewater treatment, NDMA has been shown to form when a variety of organic nitrogen precursors react with chloramines. The proposed primary mechanism involves the formation of UDMH and subsequent oxidation to form NDMA and other byproducts. A known NDMA precursor commonly found in wastewater is dimethylamine. To simplify the quantification of bulk NDMA precursors, a laboratory test known as the NDMA precursor test has been developed at UC Berkeley. Similar to the trihalomethane formation potential test, the NDMA precursor test involves adding an excess of monochloramine (e.g., 140 mg/L as Cl_2), waiting five days for NDMA to form from the NDMA precursors, and then analyzing the sample for NDMA. The results of the workshop demonstrated that there is a strong need to better understand NDMA sources, formation, and fate in wastewater treatment facilities and treatment strategies so that utilities practicing water reuse can implement appropriate NDMA control strategies cost-effectively.

Task 2 sampling activities quantified average daily NDMA concentrations entering wastewater treatment plants. Concentrations were as high as 790 ng/L of NDMA at wastewater treatment plants located in industrial areas, compared with a range of 50 to 100 ng/L of NDMA in residential areas. In general, higher concentrations of NDMA precursors were detected in industrial areas. Point-source sampling of discharges from the metal plating industry identified dithiocarbamates as NDMA precursors. Dithiocarbamates used during industrial pretreatment process contained up to 4000 ng/L of NDMA and 82,000 ng/L of NDMA precursors. Fumigants containing dimethyldithiocarbamates are sometimes applied to sewer trunklines in residential or industrial areas to control tree root growth. Elevated concentrations of NDMA (2400 ng/L) and NDMA precursors (89,000 ng/L) were measured during root control activities in the OCSD collection area.

Task 3 sampling results indicated NDMA removal could be variable during activated sludge treatment. Variable removal was observed from day to day at several facilities where sampling efforts were concentrated. For example, at the San Jose/Santa Clara Water Pollution Control Plant (SJ/SC WPCP), average daily NDMA removal ranged from 0 to 75% over four days. There was no apparent reason for this variability, such as plant upsets, changes in operating parameters, or variations in influent wastewater quality. At other treatment plants, removal during conventional air activated sludge treatment was consistently low (0–25%) during sampling events. At others, removal rates were consistently high, ranging from 50% to 90%. Variability in NDMA removal rates during secondary treatment may be due to a difference in biodegradation rates at treatment facilities; further research would be required to confirm this hypothesis.

In contrast, NDMA precursors were well-removed during conventional (air activated sludge) treatment. NDMA precursor removal rates ranged from 65% to 85%, with the exception of one treatment facility where NDMA precursor concentrations unexpectedly increased from 5400 ng/L up to 28,900 ng/L. This increase was found to be related to the use of cationic polymers that acted as NDMA precursors. Polymers were added to control foaming and improve settling during tertiary treatment. Despite the effectiveness of conventional treatment for precursor removal, enough NDMA precursors remained in secondary or tertiary effluent to form NDMA in excess of the California notification level of 10 ng/L upon chloramination.

During Tasks 3 and 4, NDMA formation during chloramination was quantified. For example, at the LACSD Whittier Narrows facility, NDMA increased by 20–540 ng/L (median increase of 120 ng/L of NDMA) in the presence of 1 mg/L of ammonia. In nitrified effluent at SJ/SC WPCP, NDMA did not increase during chlorine disinfection. However, final effluent concentrations were still in excess of the California notification level, ranging from 15 to 26 ng/L. Task 4 results illustrated that less NDMA formed when preformed monochloramines were used for disinfection, particularly at elevated pH. To preform chloramines, chlorine was first added to a dosing tank, followed by the addition of ammonia. This order of addition reduced the concentration of dichloramine that formed, reducing NDMA formation by up to 15 ng/L in the pilot-scale system.

Task 4 sample results indicated that microfiltration followed by RO could not reliably reduce NDMA below the California notification level. Microfiltration was found to be ineffective in removing NDMA; RO systems using thin-film composite membranes removed approximately 50% of the influent NDMA. A fraction of the NDMA precursors were removed during microfiltration (ranging from 12% to 95%). However, NDMA precursors were removed well by RO; NDMA precursor concentrations were similar to NDMA concentrations measured in RO effluent.

Typically, UV treatment systems are used to meet the California notification level. The photolysis model developed during Task 5 can be used to predict NDMA effluent concentrations or to predict reactor size and power consumption to meet a given NDMA effluent concentration. On average, model predictions agreed fairly well with empirical pilot study results, predicting the same range of NDMA effluent concentrations and electrical energy per unit order of NDMA destruction. Since CalDHS is considering requiring certain utilities to implement UV and H_2O_2 treatment to provide an additional treatment barrier for unregulated compounds, the model was used to predict percent removal of typical low molecular weight organic compounds reacting at diffusion-controlled rates with hydroxyl radicals. The model demonstrated that low H_2O_2 concentrations on the order of 1–5 mg/L would result in 15–80% removal of these organic compounds but would not improve NDMA removal.

Results from the Project Addendum quantified NDMA formation during disinfection in nonpotable reuse systems. The median concentration of NDMA formed during disinfection in systems using chloramines was 340 ng/L, compared to a median of less than 10 ng/L in systems where free chlorine was used in the absence of ammonia. In systems that did not practice nitrification, a direct relationship was also observed between the concentration of NDMA formed after disinfection and the concentration of total NDMA precursors present. At the chlorine doses used in these nonpotable systems, approximately 10–20% of total NDMA precursors were converted to NDMA.

PROJECT CONCLUSIONS

Project findings have led to some insights for utilities addressing NDMA. Utilities that do not have advanced treatment capabilities but need to reduce NDMA concentrations in their effluent may be interested in source control measures such as industrial pretreatment programs or permit restrictions on select industrial dischargers. This may be an effective strategy at wastewater treatment facilities where NDMA is not well-removed during conventional treatment. More research is needed to identify ways to improve NDMA removal during conventional treatment; however, one obvious question is whether polymers used within the treatment plant are acting as NDMA precursors.

Facilities with advanced treatment capabilities typically use MF-RO and/or UV treatment. This treatment train has been shown to be effective in removing NDMA and NDMA precursors. NDMA can be removed by UV treatment. The UV photolysis model enables utilities to quickly gauge the effects of water quality and addition of hydrogen peroxide on UV treatment system performance and operating costs. Since NDMA precursors are removed well by the MF-RO system, NDMA will not form if the final effluent is subjected to chloramination.

To reduce NDMA formation prior to UV treatment, the most effective strategy is for utilities to avoid chloramination by practicing nitrification prior to the addition of free chlorine. If this is not a viable control strategy, the utility may be able to preform monochloramine in a way that reduces dichloramine formation (adding chlorine to nitrified wastewater followed by the addition of ammonia). After adjusting for the difference in hydraulic retention time between pilot-scale and full-scale systems, pilot-scale results indicate that utilities preforming monochloramines may be able to reduce NDMA formation by approximately 10–35 ng/L. Other options include reducing concentrations of NDMA precursors by implementing advanced treatment, lowering the chloramine dose without compromising their ability to meet microbial targets, if possible, and using an alternative process for disinfection, such as UV treatment.

The findings presented in this report are significant to the water industry. The information will provide utilities practicing water reuse with a scientific framework for managing NDMA at wastewater treatment plants and assessing the need for additional testing, potential improvements to existing treatment processes, and the need for advanced treatment.

CHAPTER 1

INTRODUCTION

1.1 BACKGROUND

N-Nitrosodimethylamine (NDMA) is a potent probable human carcinogen (U.S. EPA, 1991). Researchers have been aware of the health effects of NDMA and related nitrosamines since the 1970s (Mirvish, 1975; NTP, 2005). NDMA was first detected in treated drinking water supplies in Ontario, Canada, in 1989 (MOEE, 1994). Follow-up sampling established that very low levels (<10 ng/L) of NDMA formed within the drinking water treatment plant. In 1998, NDMA was also detected in municipal drinking water supply wells in Sacramento, CA, and the San Gabriel Valley of California in connection with past industrial activities. On the basis of potential human health risks, the California Department of Health Services (CalDHS) set a notification level (formerly known as an action level) for NDMA of 10 ng/L (parts per trillion).[1] The established formation of NDMA during wastewater treatment and the documented persistence of NDMA in groundwater have raised a series of issues related to the long-term impact of reinjection of treated wastewater into drinking water aquifers.

1.2 PROJECT MOTIVATION

Recent research has shown that NDMA can form during water and wastewater treatment when organic nitrogen precursors react with chloramines (see Mitch et al., 2003b, for a review). NDMA concentrations in wastewater effluents exceeding regulatory guidance levels (e.g., the California notification level) are of particular concern whenever wastewater effluent is indirectly reused as a potable water supply. Indirect potable water reuse has become the leading source of new water resources in regions with fully allocated water supplies (Recycled Water Task Force, 2003). In addition, unplanned indirect potable water reuse is common in inland areas where wastewater effluent accounts for a significant fraction of the flow of surface waters (NRC, 1998). In response to NDMA detections in wastewater effluent from conventional and advanced treatment facilities, CalDHS included NDMA monitoring requirements in their draft groundwater recharge and reuse criteria (CalDHS, 2003). The presence of NDMA and other nitrosamines in water produced by advanced treatment plants has caused delays in projects in the planning stage in California and has increased the level of uncertainty for utilities involved in water reuse projects nationwide.

1.3 PROJECT DESCRIPTION

To address research gaps associated with our understanding of NDMA formation and fate during conventional and advanced wastewater treatment and to assess the efficacy of potential control strategies, the WateReuse Foundation initiated a two-year research project (WRF-01-002) in 2001. Malcolm Pirnie assembled a team of environmental professionals to address these questions under the direction of co-principal investigators Dr. Michael C. Kavanaugh and Dr. David Sedlak from the University of California at Berkeley (UC Berkeley). The project team included staff from Malcolm Pirnie, researchers from UC

---

[1] The initial action level was set at 2 ng/L with a dilution credit of one order of magnitude (20 ng/L) allowed for facilities practicing indirect nonpotable reuse. In 2002, the action level was revised to the current level of 10 ng/L. Action levels are now known as notification levels (as of January 2005).

Berkeley, UV modeling experts from McGuire Environmental Consultants, Inc. (now McGuire Malcolm Pirnie), and staff members from the following six utilities with ongoing NDMA monitoring programs related to water reuse:

- City of San Jose, California
- City of Scottsdale, Arizona
- Los Angeles County Sanitation District, California
- Orange County Sanitation District, California
- Orange County Water District, California
- West Basin Municipal Water District, California

The project team prepared a research plan addressing several aspects of NDMA and its behavior during conventional and advanced wastewater treatment. This plan was reviewed and approved by the Project Advisory Committee at the start of the project. Research objectives were divided into six key tasks as follows:

Task 1: Conduct a workshop to assess the state of knowledge on NDMA sources, fate, and control;

Task 2: Assess the importance of industrial sources of NDMA and NDMA precursors;

Task 3: Assess the removal of NDMA and NDMA precursors in conventional wastewater treatment plants;

Task 4: Assess the removal of NDMA and NDMA precursors in advanced wastewater treatment plants;

Task 5: Develop and validate a model for the efficacy of UV treatment systems for NDMA; and

Task 6: Perform project reporting and outreach.

1.4 OVERVIEW OF REPORT

Project tasks provide the framework for the organization of this report. Chapter 2 presents the results of the group’s assessment on the state of knowledge on NDMA prior to the start of the project (Task 1). This chapter also contains the results of studies published while this project was ongoing.

Chapter 3 focuses on the importance of industrial sources of NDMA and NDMA precursors (Task 2). Background information, study design, and the results of project team investigations are contained in this chapter.

Chapter 4 describes the typical fate of NDMA and NDMA precursors during conventional wastewater treatment (Task 3).

Chapter 5 describes the formation and removal of NDMA and NDMA precursors during advanced treatment, as well as control options for utilities (Task 4).

Chapter 6 presents the results of efforts to model NDMA removal in UV treatment systems (Task 5).

Chapter 7 presents the results of the project team’s investigation of NDMA occurrence and formation in nonpotable water reuse systems. The team conducted a preliminary investigation of this issue because wastewater utilities may need to address NDMA in nonpotable water reuse systems due to the potential for NDMA used in such systems to enter potable water supplies. This task is beyond the original project scope presented in the original research proposal but was addressed by the project team at no additional cost to the WateReuse Foundation.

Chapter 8 provides a summary of the main project findings presented in Chapters 3 through 7. In addition, this chapter discusses various strategies for controlling NDMA at wastewater treatment plants.

Chapter 9 contains a list of publications and other data referenced in this report.

Appendix A summarizes the project team’s communication of results through outreach and reporting (Task 6). Appendix B contains the project sampling plan and quality assurance/quality control (QA/QC) procedures. Appendix C consists of an electronic summary of all analytical data collected during the project. Appendix D includes a copy of the UV photolysis model.

CHAPTER 2

STATE OF KNOWLEDGE ON NDMA

2.1 BACKGROUND

Although NDMA has been a concern to the public health community for over 30 years (Mirvish, 1975; NTP, 2005), it has not been a major issue for water utilities until recently. Since the state of knowledge on NDMA in water and wastewater systems was rapidly evolving at the time of the proposal submission, the original research plan included a task to summarize recent research findings on NDMA prior to the start of the project (Task 1: Conduct a workshop to assess the state of the art on NDMA sources, fate, and control).

In March 2002, the research team held a project kickoff workshop in California to review the latest NDMA research findings, analytical practices, and ongoing efforts to control NDMA in conventional and advanced wastewater treatment systems. The kickoff workshop provided a foundation of current scientific knowledge and practical experience that enabled the research team to refine the project scope of work and research objectives. During the course of the project, team members continued to communicate their findings and stay abreast of the latest NDMA publications and conference presentations. This ensured that the project direction reflected the most relevant research needs. A general overview of the current state of knowledge pertaining to NDMA fate and formation in wastewater treatment and water reuse systems is summarized in this chapter to provide background for the project approach, findings, and recommendations for control strategies. The review addresses sources of NDMA in wastewater, formation and fate during conventional and advanced wastewater treatment, and subsurface fate and transport.

2.2 OVERVIEW OF NDMA

NDMA is a small, polar molecule (log $K_{ow} = 0.57$) that is highly water soluble (100 g/L at 20 °C). In the 1960s, the compound was classified as a potent class B2 (animal) carcinogen. It belongs to a family of nitrosamines with similar carcinogenic potencies (ATSDR, 1989). The chemical structure of NDMA is shown in Figure 2-1.

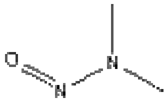


Figure 2-1. Chemical structure of NDMA.

CalDHS currently (2005) has a notification level of 10 ng/L of NDMA. The notification level was referred to as an action level prior to 2005. The Ontario Ministry of the Environment and Energy in Canada has set an interim standard of 9 ng/L of NDMA in drinking water. While the United States Environmental Protection Agency (U.S. EPA) has not yet developed a maximum contaminant level (MCL) and has not listed NDMA as a candidate for MCL development, U.S. EPA risk assessment results estimate that the 10^{-6} cancer risk to humans corresponds to 0.7 ng/L of NDMA in drinking water (U.S. EPA, 1991). U.S. EPA has set low clean-up levels for NDMA at hazardous waste sites such as Aerojet, Rancho Cordova, CA (2 ng/L) (U.S. EPA, 2001). U.S. EPA has also designated NDMA as a priority toxic pollutant for inland surface waters and enclosed bays and estuaries in California with implications for utility monitoring programs (CFR, 2000).

There is currently no regulatory-approved method for measuring NDMA at low levels in drinking water. However, CalDHS has published analytical guidelines and has participated in round-robin testing exercises with commercial, utility, and governmental laboratories (CalDHS, 2005a). The state-of-the-art analytical method for NDMA consists of liquid-liquid extraction, evapoconcentration, gas chromatography (GC), and mass spectroscopy (MS) followed by low-resolution chemical ionization or high-resolution electron impact mass spectroscopy. Deuterated NDMA (NDMA-d6) is added as an isotopic dilution surrogate standard for quality control (CalDHS, 2005a). Using this method, the reportable detection limit for NDMA analysis in samples with relatively low concentrations of organic matter is approximately 2 ng/L (Fitzsimmons, 2004, personal communication). The detection limit often is higher in untreated wastewater and wastewater effluent due to interference from organic matter and suspended solids.

2.3 IMPACTS OF NDMA ON WATER RECYCLING

Controlling NDMA concentrations in wastewater effluent is a significant concern for utilities practicing indirect potable water reuse, especially in California. In May 2000, two wells operated by the Orange County Water District (OCWD) were shut down due to the detection of 30 to 40 ng/L of NDMA associated with nearby reinjection of water produced by OCWD’s advanced treatment plant. Also in 2000, the Sanitation Districts of Los Angeles County (LACSD) detected 30 to 90 ng/L of NDMA in wastewater effluent prior to blending and discharge to an infiltration basin used to recharge groundwater. In the city of San Jose, CA, plans to construct a nonpotable water reuse pipeline to deliver water to a proposed power plant were temporarily stopped by a lawsuit alleging that NDMA in the irrigation water had the potential to percolate into groundwater and contaminate the aquifer (Rosenbaum, 2001). The presence of NDMA in wastewater effluent has increased the level of uncertainty among utilities with ongoing water reuse projects.

Typical NDMA concentrations detected in various water sources are shown in Figure 2-2. Surface water that is not impacted by wastewater discharges or industrial waste typically has low levels of NDMA (<10 ng/L). Between 2000 and 2002, the Province of Ontario sampled raw water and finished drinking water from 159 utilities. Out of 1021 samples, only 23 of the finished waters (2%) had concentrations greater than 9 ng/L (MOE, 2004), and in most cases when NDMA was detected (detection limit, 5 ng/L), NDMA concentrations were higher after treatment. This is in agreement with a recent CalDHS survey of 19 different surface water treatment plants. CalDHS reported 10 out of 30 detections (detection limit, 1 ng/L) with an average detection of 2.2 ng/L and a maximum concentration of 9.4 ng/L in the finished drinking water (CalDHS, 2002).

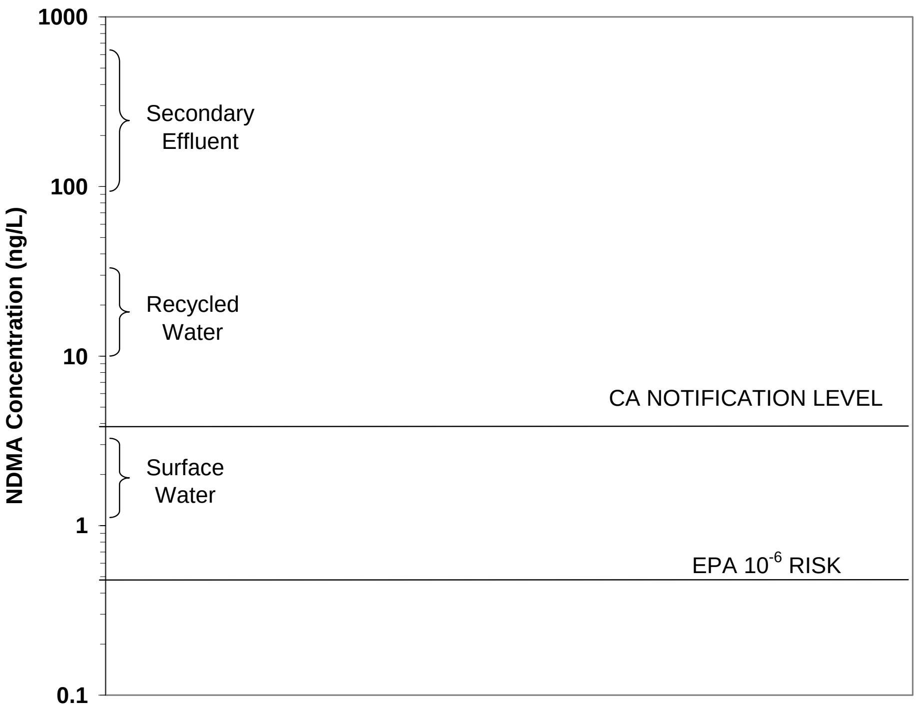


Figure 2-2. Typical NDMA concentrations in surface water sources and wastewaters.

In contrast, secondary wastewater effluent typically contains 10 to 1000 ng/L of NDMA, up to two orders of magnitude higher than surface water. Even after advanced treatment, such as microfiltration (MF) followed by reverse osmosis (RO) and/or UV disinfection, treated and chlorinated wastewater commonly contains between 10 and 100 ng/L of NDMA, well above California's notification level (West Basin, unpublished data).

High NDMA concentrations in wastewater effluent are of concern due to the potential for NDMA to enter drinking water supplies during intentional or unintentional potable water reuse. Indirect potable water reuse has become the leading source of new water resources in many regions with fully allocated freshwater supplies (Recycled Water Task Force, 2003). Currently, California has one of the most extensive water reuse programs in the world. California reuses 19.5 m^3/s (0.5 million acre ft/year) through planned water reuse projects (Recycled Water Task Force, 2003). This is equivalent to approximately 10% of the total annual volume of municipal wastewater effluent in California (Recycled Water Task Force, 2003). Primary uses of this water include agricultural irrigation (48%), landscape irrigation (20%), groundwater replenishment (12%), industrial supply (5%), seawater intrusion barriers (3%), and other uses (12%). California has the potential to increase water recycling to a total of 1.5 million acre ft/year by 2030 at an estimated cost of $11 billion (2000 $) (Recycled Water Task Force, 2003).

Water utilities across the nation have similar programs for nonpotable water reuse. Other states, including Arizona, Florida, Virginia, Colorado, South Carolina, and Texas, have implemented indirect water reuse projects that could be subject to NDMA regulations in the future. In addition, unplanned indirect water reuse is common in inland areas where treated wastewater is discharged to surface waters. For example, in 1980, Swayne et al. estimated that 7.7 million people in the United States were served by utilities using in excess of 50% wastewater during low river flow conditions (Swayne et al., 1980).

2.3.1 California Draft Recharge Criteria

The state of California is in the process of developing recycled water and drinking water regulations to update the existing California Code of Regulations and supplement pertinent sections of the California Water Code. CalDHS drafted a report on Groundwater Recharge and Reuse Criteria in July 2003 (updates to Title 17 and 22 of the California Code of Regulations) but has not begun the final rulemaking process (CalDHS, 2003). California's Groundwater Recharge and Reuse Criteria are carefully watched by regulators in the United States and abroad. It is likely that California's actions will influence policies in other regions nationally and internationally.

Among other requirements, the draft Title 22 regulations specify quarterly monitoring for select unregulated contaminants, including priority toxic pollutants such as NDMA (CFR, 2000), lead, copper, and a listed subset of chemicals with notification levels. Once a year, after draft requirements have been finalized, utilities will be required to monitor for a short list of pharmaceuticals, endocrine-disrupting chemicals, and other chemical indicators of municipal wastewater presence. Positive results will be reported on a monthly basis to the Regional Boards in California. Annual and five-year reports will be submitted to the Regional Boards, CalDHS, and downgradient drinking water systems. Regional Boards may reduce monitoring frequency based on preliminary results.

2.3.2 NDMA Monitoring Programs

Due to Title 22 monitoring requirements, many utilities in California are monitoring for NDMA. Title 22 requirements list other nitrosamines, including nitrosodiethylamine (NDEA) and nitrosopyrrolidine, as desired or optional compounds for monitoring. California has also developed a notification level for NDEA (10 ng/L) (CalDHS, 2005b).

While California is the only state requiring utilities to monitor for NDMA at low levels, the state of Arizona has recently started requiring NDMA monitoring under the state-administered National Pollutant Discharge Elimination System permits. The recommended maximum water quality concentration is 30 ng/L of NDMA based on an exposure route of partial body contact. However, low detection limits are not required. From a practical standpoint, most commercial laboratories can achieve reporting limits ranging from 1000 to 10,000 ng/L using routine GC/MS techniques not specifically targeting nitrosamines.

2.4 NDMA FORMATION MECHANISMS

NDMA can form during municipal wastewater treatment and drinking water treatment. Two NDMA formation mechanisms have been hypothesized: (1) the formation and subsequent oxidation of unsymmetric dimethyl hydrazine (UDMH) and (2) nitrosation, the formation of N_2O_3 from HNO_2, which then reacts with a secondary amine such as dimethylamine (DMA) to form NDMA. While the nitrosation reaction accounts for NDMA formation in foods and in several consumer products, the formation and oxidation of UDMH is the primary mechanism, as discussed below, that leads to NDMA formation during water and wastewater treatment when chlorine is used.

The formation of NDMA through chlorination reactions that occur in wastewater disinfection systems was first demonstrated in 2002 (Choi and Valentine, 2002; Choi et al, 2002; Mitch and Sedlak, 2002a). In the first step of this reaction, hypochlorite is added to ammonia-containing water, forming monochloramine, which reacts with an organic nitrogen precursor such as DMA to form UDMH (eq 1).

$$NH_2Cl + NH(CH_3)_2 \rightarrow NH_2N(CH_3)_2 + HCl \tag{1}$$

The UDMH then reacts with monochloramine or another oxidant to form a number of intermediates. NDMA is one of several final products of competing reactions with a yield generally less than 5%; however, the actual yield depends on reaction conditions (Fig. 2-3). Other products include dimethylcyanamide (DMC), dimethylformamide (DMF), formaldehyde dimethylhydrazone (FDMH), and formaldehyde monomethylhydrazone (FMMH). More details on this formation mechanism are contained in the article by Mitch and Sedlak (2002a).

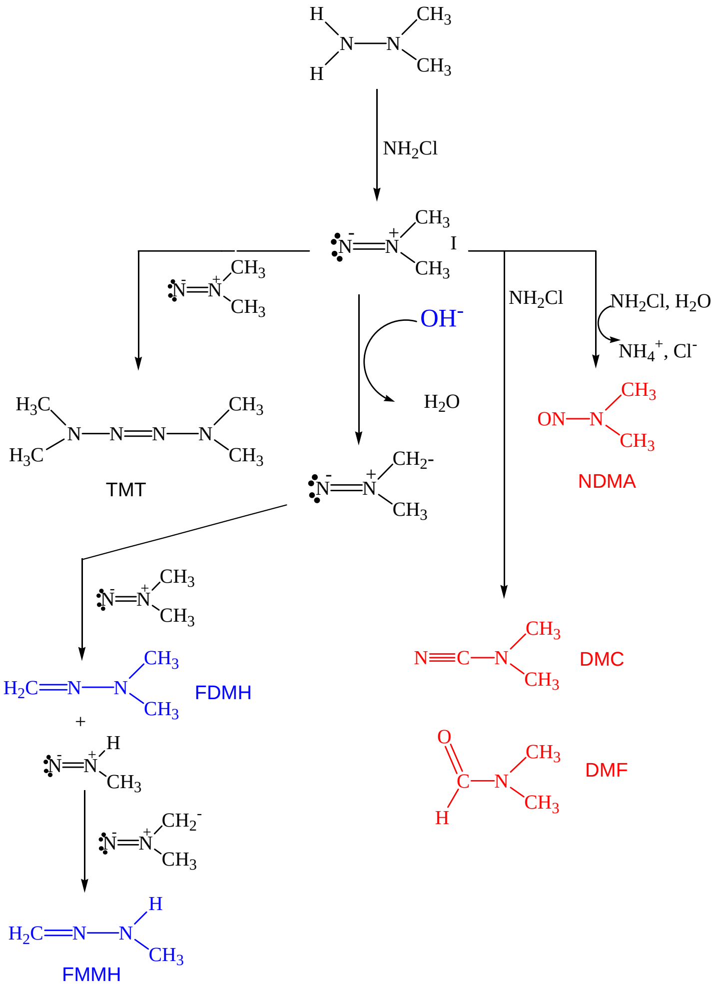


Figure 2-3. Mechanism of NDMA formation via UDMH formation and oxidation in chlorinated water supplies (Mitch and Sedlak, 2002a).

Nitrosation also can result in NDMA production. During nitrosation nitrite is acidified, forming nitrosyl cation (NO^+). The nitrosyl cation then reacts with an amine, such as DMA, to form NDMA (Mirvish, 1975):

$$NO_2^{\,-} + 2H^+ \Leftrightarrow H_2O + NO^+ \tag{2}$$

$$NO^+ + (CH_3)_2NH \Rightarrow (CH_3)_2NNO + H^+ \tag{3}$$

Nitrosation occurs slowly under conditions typical of a water or wastewater environment. The second-order rate constant for NDMA formation is $1.5 \times 10^{-5}\ M^{-2}\ s^{-1}$. For example, at neutral pH in the presence of 6 mg/L (100 µM) nitrite and 6 mg/L (100 µM) of DMA, which are typical wastewater conditions, a negligible amount (only 10^{-12} ng/L of NDMA) is predicted to form over 24 h (Mitch and Sedlak, 2002a). The mechanism is therefore too slow to account for NDMA formation in wastewater. Furthermore, nitrite would be oxidized to nitrate with a half-life less than 1 s when hypochlorite is present in wastewater. Nitrosation can occur in the acidic environment of the stomach when nitrite is present (Shapley, 1976). Nitrosation is believed to be responsible for NDMA formation in vegetables, fish, and meat cured with nitrite, as well as formation in tobacco smoke.

The publication of studies indicating NDMA formation via UDMH oxidation (Choi and Valentine, 2002; Mitch and Sedlak, 2002a) raised questions about wastewater chlorination practices. Since NDMA forms from monochloramines and organic nitrogen precursors such as DMA, it seems likely that limiting the concentration of these precursors and the amount of chlorine and ammonia present during disinfection could limit NDMA formation. Mitch and Sedlak (2002a) recommended removing ammonia from wastewater prior to adding chlorine (i.e., through nitrification) or using alterative disinfectants such as UV or ozone. However, these hypotheses had not been tested in full-scale treatment systems.

2.5 NDMA PRECURSORS

DMA is the simplest organic nitrogen precursor for NDMA. DMA is found in urine, feces, algae, and plants (Tricker et al., 1994). It is a breakdown product of choline [$^+N(CH_3)_3CH_2CH_2OH$], which is typically found in human and other animal waste products (Zeisel et al., 1985). DMA can also be found in herbicides (NIH NLM, 2004).

Typical DMA concentrations in raw sewage reportedly range from 20 to 80 µg/L (Mitch and Sedlak, 2002b). However, only a small fraction (approximately 10%) of the NDMA formed in wastewaters and natural waters is attributable to DMA (Gerecke and Sedlak, 2003; Mitch et al., 2003a). The majority of organic nitrogen NDMA precursors have not yet been identified (Mitch and Sedlak, 2004).

Researchers at UC Berkeley have developed an analytical test to quantify the organic nitrogen-containing NDMA precursors present in water or wastewater streams (Mitch et al., 2003a). The test is referred to as the NDMA precursor test and is similar to the trihalomethane (THM) formation potential test (APHA, 1998). The NDMA precursor test has not yet been approved by U.S. EPA. Currently, there is no standard method for measuring NDMA precursors. One of the objectives of this study was to verify the reproducibility of this analytical method in practice at different laboratories.

As part of the NDMA precursor test, water samples that may contain a variety of organic nitrogen precursors are subjected to a relatively high dose of preformed monochloramine (i.e., 140 mg/L as Cl_2) and allowed to react for several days, enabling the NDMA reaction to go to completion. The NDMA concentration in the sample is then measured. NDMA precursors are determined by subtracting the initial NDMA concentration from the NDMA precursor test results. Since an excess of chloramines is added, the NDMA reaction will be limited by the concentration of organic nitrogen-containing NDMA precursors.

Although it cannot be used directly as a measure of NDMA production during effluent disinfection, the NDMA precursor test is useful for quantifying bulk organic nitrogen precursors and comparing the amount of NDMA precursors in different water samples to each other regardless of actual chlorination conditions. Typical total NDMA precursor values measured in untreated wastewater and secondary effluent range from 1000 to 10,000 ng/L (Mitch et al., 2003b).

Samples from municipal wastewater treatment plants contain both dissolved and particle-associated nitrogen precursors (Mitch and Sedlak, 2004). NDMA precursor tests were conducted after passing wastewater samples through filters with various pore sizes. Results indicated that NDMA precursors are typically either greater than 0.7 µm (approximately the size of a bacterium) or are low molecular weight, dissolved molecules (less than 3000 g/mol). A distribution of precursor particle sizes is shown in Figure 2-4.

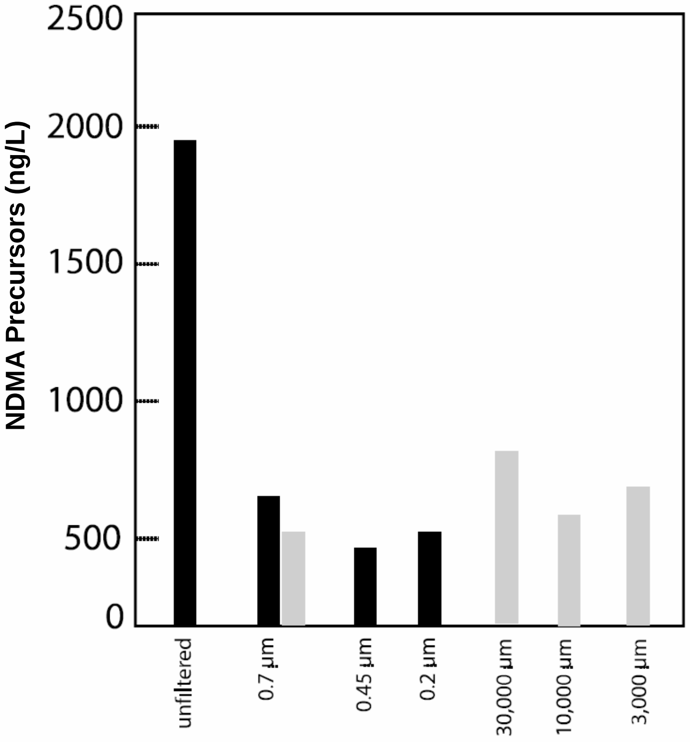


Figure 2-4. Size fractionation of organic nitrogen precursors. Black bars, day 1 samples; gray bars, day 2 samples. (Adapted from Mitch and Sedlak, 2004.)

Low molecular weight NDMA precursors in wastewater effluent consist of substances other than DMA. Compounds that also react with monochloramine to form NDMA include aliphatic tertiary amines, such as trimethylamine (Mitch and Sedlak, 2002a), molecules with dimethylamine functional groups, such as dimethylethanolamine (Mitch and Sedlak, 2004), dimethyl amides (Mitch and Sedlak, 2004), and organic amines (Wolfe and Olson, 1986). The fungicide Thiram (tetramethylthiuram disulfide) and the herbicide 2,4-D have also been identified as NDMA precursors (Graham et al., 1996).

Particle-associated NDMA precursors appear to be related to polymers used in wastewater treatment. In drinking water treatment plants, a polymeric diallyl-dimethyl ammonium cationic [poly(DADMAC)] polymer used for flocculation was found to be an NDMA precursor (Child et al., 1996; Najm and Trussell, 2001; Najm et al., 2004; Wilczak et al., 2003). Two types of cationic polymers used in wastewater treatment plants (an ADAMQUAT polyacrylamide and a DMA-based polyacrylamide) were tested by Mitch and Sedlak (2004) and found to be NDMA precursors.

2.6 INDUSTRIAL SOURCES OF NDMA TO WASTEWATER TREATMENT FACILITIES

NDMA in wastewater effluent can also originate in untreated wastewater. NDMA can form during manufacturing processes, often unintentionally, and it can impact wastewater effluent if those wastes are discharged to the sanitary sewer. NDMA is present in lubricants, copolymers, antifreeze, and rubber manufacturing and is also a breakdown product of the rocket fuel component UDMH. Rocket fuel components were responsible for NDMA detections as high as 400,000 ng/L in groundwater at the Aerojet site, Rancho Cordova, CA (CalDHS, 2005c; MacDonald, 2002). Aerojet site detections and the subsequent closure of nearby municipal wells in 1998 spawned an interest in NDMA occurrence in drinking water and prompted the state of California to institute monitoring requirements and develop a state action level. Follow-up research studies showed that NDMA could also form during water treatment from the reaction of organic nitrogen precursors with chlorine or chloramines. The main organic precursor identified was DMA. While NDMA formation is a minor side reaction of DMA–chlorine interactions (<1%), the yield can be high enough to exceed NDMA levels of concern.

NDMA may also be present in industrial wastes that are discharged to wastewater treatment plants. Although there is no evidence that NDMA is still manufactured in the United States, commercial production occurred from the mid-1950s until 1976 (NTP, 2005). NDMA was primarily used as an intermediate in the production of liquid rocket fuel and was present at approximately 0.1% as an impurity in UDMH. NDMA has been detected in groundwater in connection with rocket fuel use at several contaminated sites (Rocky Mountain Arsenal, CO; Lockheed Martin facility in Waterton, CO; Edwards Air Force Base, CA; Aerojet site in Rancho Cordova, CA; and San Gabriel Valley in southern California).

NDMA is also used in consumer and industrial applications, including nematocides, rubber and polymer plasticizers, high-energy batteries, and the fiber and plastics industry, as an antioxidant, softener of copolymers, and an additive to lubricants (NTP, 2005). NDMA forms as an impurity in cutting fluids and rubber processing. Groundwater is contaminated beneath a UniRoyal factory in Elmira, ON, Canada, where rubber and agrichemicals were manufactured. NDMA was detected at levels as high as 1.5 mg/L (1,500,000 ng/L) at the site and as high as 3000 ng/L in nearby municipal drinking water wells (Lem, 2003).

Studies conducted by the Orange County Sanitation District (OCSD) have demonstrated the presence of NDMA in raw sewage in residential and industrial areas. Spikes in influent wastewater NDMA concentrations have been attributed to batch discharges from industrial plating operations, circuit board manufacturing, carpet dyeing, and use of herbicides such as metam sodium (dimethyldithiocarbamates) in sewers for root control (OCSD, 2002). Studies at the LACSD also have demonstrated high concentrations of NDMA in used antifreeze and drum recycler discharge (Carr et al., 2003). It is possible that these sources contribute to NDMA in untreated wastewater.

2.7 REMOVAL AND DESTRUCTION

NDMA is very stable in aqueous solution. It is resistant to air stripping and sorption, due to the molecule’s polarity and high solubility. It is also resistant to biodegradation. The most common way to treat NDMA is through photolysis. NDMA will break down in sunlight with a half-life of several hours in shallow waters under typical mid-day conditions. The transformation of NDMA is even faster in the presence of UV light, because the nitrogen-nitrogen bond of NDMA is easily photolyzed by UV light within a range of 175–275 nm, with an optimal wavelength of 228 nm (Sharpless et al., 2003). After first discovering NDMA in effluent from Water Factory 21, OCWD used exposure to sunlight to reduce NDMA concentrations prior to installing a UV system.

Due to the low (nanograms per liter) concentrations of NDMA desired in the finished water, UV and UV–H_2O_2 treatment systems must be operated at a higher dose than is typically used for disinfection. For example, *Cryptosporidium* destruction requires a dose of approximately 8–12 mJ/cm^2, but NDMA destruction may require 600–800 mJ/cm^2 (Modifi et al., 2000). The required energy is a factor of UV reactor design (such as the dimensions and lamp specifications), water quality parameters (competitive absorbers for UV), and influent NDMA concentrations and removal requirements. Because of the high energy requirements, UV treatment is an expensive technology to add onto full-scale treatment facilities.

Alternative treatment technologies for NDMA removal have not been successful. For example, granular activated carbon (GAC) has been shown to have relatively little adsorption capacity for NDMA (Fleming et al., 1996). Furthermore, other researchers have reported that GAC can promote nitrosamine formation (Dietrich et al., 1986; DiGiano, 1986). NDMA also can be destroyed by other OH radical-based advanced oxidation processes, such as Fenton’s reagent (Fe/H_2O_2) (Kommineni et al., 2003; Shaw Environmental Inc., 2004), or by granular zero-valent iron or nickel-enhanced iron reduction (Gui et al., 2000). However, neither technology is cost-effective for use in full-scale municipal wastewater treatment plants. Biodegradation of NDMA can occur by bacteria that express monooxygenase enzymes; however, biodegradation pathways for NDMA transformation are still not well understood (Sharp and Alvarez-Cohen, 2002).

2.8 FATE AND TRANSPORT IN THE SUBSURFACE

The practice of water reuse is growing in the United States. Regulatory agencies are beginning to address the possibility of aquifer contamination resulting from groundwater replenishment. Reinjection of highly treated wastewater effluent or percolation of wastewater effluent (i.e., soil aquifer treatment) could contaminate aquifers with NDMA and other unidentified chemicals in tertiary treated wastewater. This is particularly an issue in the arid western portion of the United States, where this practice is used.

When surface spreading or irrigation is employed, photolysis may destroy some of the NDMA. In areas where there is limited sunlight or where rapid percolation through the soil occurs, NDMA may penetrate through the vadose zone into the aquifer. Despite advanced treatment with membranes, such as reverse osmosis, NDMA may still pose a problem because it is not completely removed by this process. In 1998, monitoring near an injection point in southern California revealed NDMA levels as high as 150 ng/L. In 2000, at a second southern California site, NDMA detections in the range of 30 to 70 ng/L were found in wells near the injection point (CalDHS, 2005c). The fate of NDMA in the subsurface is currently a topic of research funded by groups such as the WateReuse Foundation (WateReuse Foundation, 2002).

2.9 DATA GAPS AND PROJECT APPROACH

In light of recent findings and concerns, utilities that are practicing water reuse may be faced with questions such as the following:

- Is the majority of NDMA found in wastewater effluent forming within the plant or entering the plant in raw sewage?
- If NDMA is entering in untreated wastewater, are the levels of concern due to industrial discharges? Are NDMA concentrations fairly constant throughout the day or do concentrations spike and decline due to the periodic occurrence of industrial discharges?
- Will the majority of NDMA be removed during conventional treatment? What fraction of NDMA precursors will be removed during conventional treatment? Does removal depend on the type of secondary treatment?
- How can utilities alter their treatment or disinfection process to reduce NDMA formation? What role does the choice of disinfectant (chlorine, chloramines) play?
- If advanced treatment is already being considered, which treatment options remove NDMA? How reliable are these options? What is the approximate unit cost in relation to NDMA influent concentrations and percent NDMA removal for different scales (volumes) of treatment?
- Some wastewater utilities are currently producing nonpotable-quality water for irrigation purposes. In the foreseeable future, will they be required to use advanced treatment such as microfiltration, reverse osmosis, UV treatment, or advanced oxidation to control NDMA?
- What alternatives are there for decreasing NDMA concentrations in wastewater effluent?
- Are there other sources of NDMA that have the potential to contaminate aquifers?

CHAPTER 3

SOURCES OF NDMA ENTERING MUNICIPAL WASTEWATER TREATMENT FACILITIES

3.1 BACKGROUND

Driven by a need to meet the low California notification level of 10 ng/L for NDMA in their final wastewater effluent, utilities practicing indirect nonpotable reuse have recently begun monitoring for NDMA. NDMA is commonly detected in wastewater influent. At some treatment plants, such as Plant 1 in the OCSD, influent NDMA concentrations typically are roughly equivalent to effluent concentrations (~100 ng/L) and far exceed the California notification level of 10 ng/L. Although it may be possible to improve NDMA removal during advanced treatment or decrease NDMA formation within the plant, utilities are also interested in the potential benefits of source control (i.e., through pretreatment programs or permit restrictions on NDMA or NDMA precursors discharged to the sewer within their collection area). If certain industries or dischargers were contributing a significant fraction of the NDMA or the NDMA precursors, control methods such as pretreatment, product reformulation, product substitution, or process substitution would reduce NDMA concentrations entering the treatment plant and could enable utilities to meet their NDMA effluent requirements.

In response to this issue, the project scope included a task to assess the importance of industrial sources of NDMA and NDMA precursors (Task 2). The scope included cooperation with OCSD's source control program and other wastewater facilities to investigate the following:

- Concentrations of NDMA and NDMA precursors entering wastewater treatment plants in domestic sewage.
- Concentrations of NDMA and NDMA precursors entering wastewater treatment plants in industrial areas.
- The percentage of influent NDMA and NDMA precursors attributable to industrial discharges.
- Identification of other point sources of NDMA and NDMA precursors to wastewater influent.
- Potential benefits of source control at facilities like OCSD's Plant 1.
- Key factors for utilities to consider before undertaking a rigorous source control program for NDMA.

3.2 METHODS

To address these research topics, the project team collected influent wastewater samples from seven different publicly owned treatment works. The hydraulic capacity of the plants ranged in size from 15 to 167 million gal/day (MGD); a spectrum of sewage composition was represented, ranging from less than 2% industrial to 18% industrial wastewater by volume. Treatment plant characteristics are shown in Table 3-1.

Table 3-1. Summary of Wastewater Characteristics and Processes at Selected Wastewater Treatment Plants[1] (Sedlak et al., 2005)

Location	Design Flow, m^3/s (MGD)	% Industrial Contribution	Secondary Treatment	Advanced Treatment	Disinfection
Inland Empire RP-1	1.9 (44)	<2	Activated sludge	NDN	HOCl
Whittier Narrows	0.66 (15)	18	Activated sludge	NDN	HOCl
OCSD Plant 1	2.5 (58)[b]	5	Activated sludge	None	HOCl
OCSD Plant 2	3.9 (90)[b]	8	O_2-activated sludge	None	HOCl
San Jose Creek West	1.3 (30)	4	Activated sludge	None/NDN[c]	Cl_2
San Jose/Santa Clara	7.3 (167)	11	Activated sludge	NDN, filtration	HOCl
Scottsdale	0.69 (16)	Unknown[d]	Activated sludge	NDN	HOCl

Note: NDN, nitrification-denitrification.

[a] The Whittier Narrows and San Jose Creek West WWTPs were operated by the LACSD.

[b] Value represents the design flow for secondary treatment. The OCSD's Plant 1 WWTP has a design flow of 4.7 m^3/s for primary treatment, and the OCSD's Plant 2 WWTP has a design flow of 7.3 m^3/s for primary treatment. Primary effluent from both WWTPs was discharged through an ocean outfall.

[c] The San Jose Creek West WWTP was operated without nitrification-denitrification before June 2003.

[d] Estimates of the industrial contribution to the Scottsdale WWTP were unavailable. However, plant operators were unaware of large metal plating or printer circuit board manufacturing facilities in the service area.

3.2.1 Sample Collection

Typically, 24-h composite samples were collected in order to minimize the effect of temporal fluctuations in wastewater composition on NDMA and NDMA precursor concentrations. The project team could then meaningfully compare results from different wastewater treatment plants without analyzing a series of grab samples from each treatment plant. By collecting 24-h composite samples, the start and end times of sample collection did not impact sample results. Composite samples were collected during the work week with the exception of two composites collected during the weekend from the San Jose/Santa Clara Water Pollution Control Plant (SJ/SC WPCP) and from the Orange County Sanitation District (11/17/02 and 9/30/02, respectively). Weekend samples were collected to test the impact of industrial activity on influent wastewater characteristics. Grab samples or 12-h composite samples were collected to test specific industrial and residential areas for NDMA and NDMA precursors, including industrial discharges and residential trunklines in the OCSD collection area. As

---

[1] Estimates of industrial contributions were provided by each wastewater utility. To obtain the estimate, the average annual flow rate of wastewater discharged to the treatment facility under industrial discharge permits was divided by the average annual flow rate through the treatment plant.

indicated by comparison of previous grab sample and composite sample results, composite samples were more representative of average daily concentrations. More information on sample collection protocol and quality assurance/quality control procedures is included in Appendix B.

3.2.2 Analytical Methods

NDMA was analyzed at the OCSD and LACSD laboratories using continuous liquid-liquid extraction or liquid-liquid extraction followed by chemical ionization, isotope dilution, and GC/MS. The reportable detection limits in secondary effluents ranged from 1 to 10 ng/L. The reportable detection limit in the more complex matrix of untreated wastewater and primary effluent ranged from 10 to 40 ng/L.

Total NDMA precursors were analyzed at OCSD, LACSD, and at UC Berkeley using the NDMA precursor test. The test consisted of adding pH buffer and a large dose of monochloramine (140 mg/L as Cl_2) to the sample and allowing the reaction of monochloramine and organic precursors to go to completion over 5 days, forming NDMA and a variety of other products. The sample was then analyzed for NDMA. A more complete description of the analytical method has been provided by Mitch et al. (2003a).

DMA was analyzed at UC Berkeley by GC/MS/MS analysis following derivatization with 4-methoxybenzenesulfonyl chloride (Mitch et al., 2003a). The detection limit for DMA was approximately 0.5 µg/L (500 ng/L). Other water quality parameters, including ammonia, nitrate, nitrite, total suspended solids, alkalinity, total organic carbon, and dissolved organic carbon, were analyzed using standard methods (APHA, 1998) at either OCSD, LACSD, San Jose/Santa Clara, or the City of Scottsdale.

3.3 RESULTS AND DISCUSSION

NDMA was detected in the influent and/or primary effluent of each treatment plant sampled in this study. Concentrations typically ranged from 10 to 400 ng/L of NDMA with a median concentration of 83 ng/L in wastewater influent and 49 ng/L in primary effluent, as shown in Table 3-2. NDMA precursors, as measured using the NDMA precursor test, ranged from 1680 to 17,900 ng/L, with a median concentration of 4570 ng/L in wastewater influent and 4700 ng/L in primary effluent (Table 3-3). DMA concentrations in influent and primary effluent ranged from 43 to 120 µg/L, with a median concentration of 78 µg/L in wastewater influent and 84 µg/L in primary effluent. This agrees with previous data published by Mitch and Sedlak, where grab samples collected from 12 wastewater treatment plants contained between 720 and 81,000 ng/L of NDMA precursors and between 30 and 100 µg/L of DMA, with one grab sample containing 660 µg/L of DMA (Mitch and Sedlak, 2004).

Although DMA is a known NDMA precursor, it does not fully explain the NDMA precursor test results. Assuming a 2.6% molar yield of NDMA from DMA during the NDMA precursor test (Mitch and Sedlak, 2004), DMA accounted for an average of 70% (from 24% to 100%) of the NDMA precursors measured in the influent or primary effluent samples. Other organic nitrogen compounds present in sewage also act as NDMA precursors (Mitch and Sedlak, 2004).

Table 3-2. NDMA Detections in Wastewater Influent and Primary Effluent

Facility	Date	Day	Influent, ng/L	Primary Effluent, ng/L
Inland Empire Reclamation Plant 1	4/7/2003	M	NS	7
	3/29/2004	M	NS	28
	3/30/2004	Tu	NS	42
	3/31/2004	W	NS	41
OCSD Plant 2	9/29/2003	M	NS	93
	9/30/2003	Tu	NS	110
LACSD San Jose Creek West	8/29/2002	Su	NS	190
	3/23/2004	Tu	NS	29
	3/24/2004	W	NS	22
City of Scottsdale Water Campus	9/28/2003	Su	130	140
	9/29/2003	M	51	73
LACSD Whittier Narrows	11/20/2002	W	54	72
	10/21/2003	Tu	62	14
	10/22/2003	W	17	13
	3/23/2004	Tu	NS	399
	3/24/2004	W	NS	272
OCSD Plant 1	9/27/2002	F	82	NS
	9/30/2002	M	179	NS
	10/1/2002	Tu	83	NS
	10/2/2002	W	88	NS
	9/29/2003	M	NS	55
	9/30/2003	Tu	NS	82
SJ/SC WPCP	11/17/2002	Su	66	NS
	11/18/2002	M	166	NS
	11/19/2002	Tu	177	NS
	11/20/2002	W	359	NS
	9/16/2003	Tu	35	31
	9/17/2003	W	104	37
MIN			17	7
MAX			359	399
AVERAGE			110	88
MEDIAN			83	49
COEFF. VARIATION			77	113

Note: NS, not sampled.

Table 3-3. NDMA Precursor Detections in Wastewater Influent and Primary Effluent

			NDMA Precursors, ng/L		DMA, µg/L	
Facility	**Date**	**Day**	**Influent**	**Primary Effluent**	**Influent**	**Primary Effluent**
Inland Empire	4/7/2003	M	NS	2497	NS	57
	3/29/2004	M	NS	5500	NS	84
	3/30/2004	Tu	NS	5300	NS	93
	3/31/2004	W	NS	4000	NS	71
OCSD Plant 2	9/29/2003	M	NS	8400	NS	NA
	9/30/2003	Tu	NS	9400	NS	NA
LACSD San Jose Creek West	8/26/2002	Th	NS	206 R	NS	NA
	8/29/2002	Su	NS	2667	NS	NA
	3/23/2004	Tu	NS	10,750	NS	89
	3/24/2004	W	NS	17,950	NS	102
City of Scottsdale Water Campus	9/28/2003	Su	3400	3800	46	48
	9/29/2003	M	2800	3600	43	43
	9/30/2003	Tu	NA	NA	48	44
LACSD Whittier Narrows	11/18/2002	M	NA	NA	69	63
	11/20/2002	W	3351	2899	NA	NA
	10/21/2003	Tu	4330	3670	NA	NA
	10/22/2003	W	1680	NS	NA	NS
	3/23/2004	Tu	NS	12,000	NS	114
	3/24/2004	W	NS	11,800	NS	79
OCSD Plant 1	9/27/2002	F	5257	NS	79	NS
	9/30/2002	M	4565	NS	82	NS
	10/1/2002	Tu	5574	NS	78	NS
	10/2/2002	W	4802	NS	82	NS
	9/29/2003	M	NS	5100	NS	NA
	9/30/2003	Tu	NS	4700	NS	NA
SJ/SC WPCP	11/17/2002	Su	5230	NS	70	NS
	11/18/2002	M	3940	NS	92	NS
	11/19/2002	Tu	6470	NS	120	NS
	11/20/2002	W	9270	NS	107	NS
	9/15/2003	M	NA	NA	76	94
	9/16/2003	Tu	6270	4130	78	110
	9/17/2003	W	3190	3110	91	120
Min			1680	2497	43	43
Max			9270	17,950	120	120
Average			4675	6383	77	81
Median			4565	4700	78	84
Coeff. of Variation			39	66	27	32

Note: NS, not sampled; NA, not analyzed for NDMA precursors or DMA R, rejected due to matrix interference.

Water quality parameters were fairly consistent among different treatment plants and over time. Organic nitrogen as N ranged from 8 to 11 mg/L. Ammonia as N ranged from 23 to 33 mg/L; nitrite as N ranged from nondetect (<0.01 mg/L) to 0.06 mg/L. Nitrate as N was nondetect (<0.05 mg/L) except at OCSD's Plant 1, where it ranged from 0.33 to 0.85 mg/L. Biochemical oxygen demand (BOD) ranged from 240 to 290 mg/L, dissolved organic carbon ranged from 35 to 90 mg/L, and total suspended solids (TSS) ranged from 228 to 340 mg/L in influent samples and from 7 to 124 mg/L in primary effluent. As expected, water quality parameters were not well-correlated with NDMA concentrations or with NDMA precursors (results not shown). Complete results are provided in Appendix A.

3.3.1 Variation in NDMA and NDMA Precursor Loading Rates over Time

From August 2000 to November 2001, OCSD conducted an investigation of NDMA concentrations entering the OCSD Plant 1 in different trunklines (OCSD, 2002). They found elevated NDMA concentrations in wastewater influent lasting 4 to 6 h (Fig. 3-1). During the day, NDMA concentrations varied up to several orders of magnitude. OCSD suspected that the temporary increases in NDMA concentration were caused by batch discharges of industrial wastewaters into the trunkline. This observation illustrates the importance of collecting 24-h composite samples to measure NDMA concentrations that are representative of daily averages.

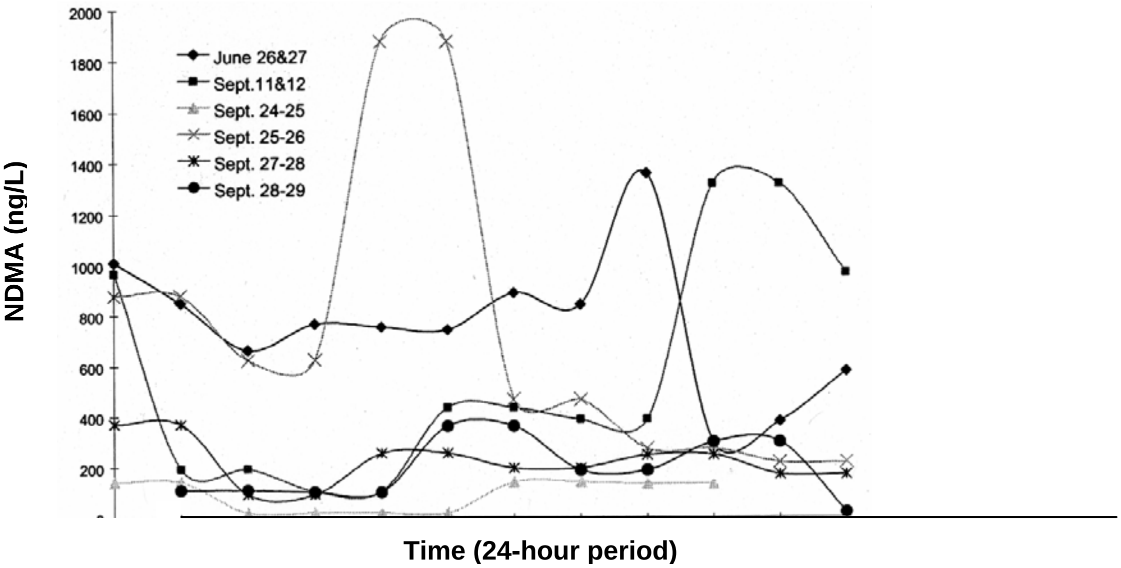


Figure 3-1. Daily variation in NDMA concentrations in a trunkline to OCSD Plant 1 (OCSD, 2002).

Since industrial discharges do not typically occur on weekends, the project team hypothesized that, on average, weekend NDMA concentrations would be lower than weekday concentrations in industrial areas. To quantify the difference, 24-h composite samples were collected on the weekend and on weekdays at SJ/SC WPCP and OCSD's Plant 1. The size of the collection system was taken into account during these experiments. For example, weekend activity at OCSD Plant 1 was captured in a Monday sample. Results from SJ/SC

WPCP are shown in Figure 3-2. Results from OCSD Plant 1 are not shown graphically; however, data are included in Table 3-2 (9/27/04 through 10/2/04).

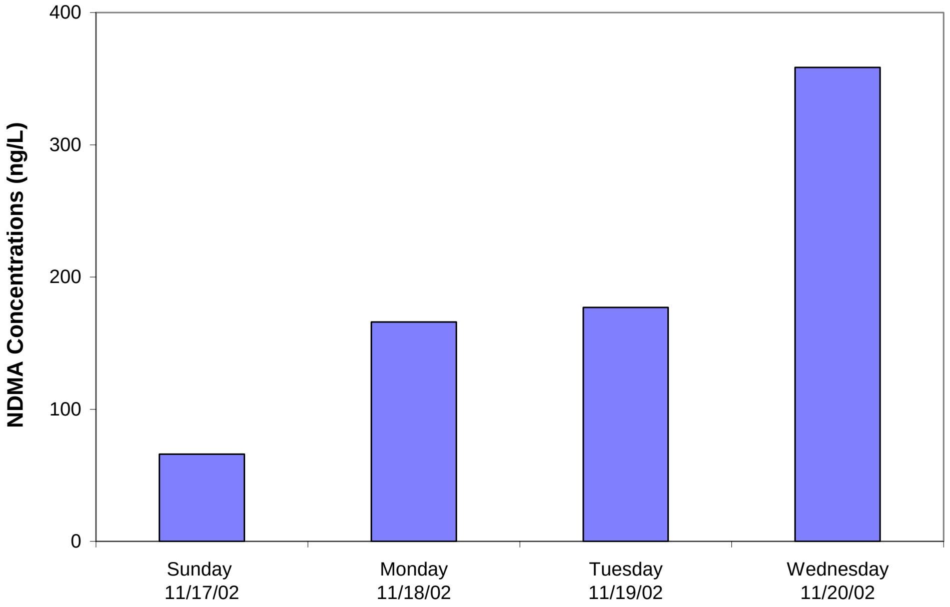


Figure 3-2. Weekly variation in NDMA concentration in SJ/SC WPCP primary effluent.

As expected, NDMA concentrations at SJ/SC WPCP were approximately 80% lower on the weekend than in the middle of the week. Concentrations on Monday and Tuesday were not as high as on Wednesday but were still elevated in comparison to the weekend sample. In contrast, data from OCSD suggested that significant industrial discharges did not occur during the week of sample collection or that industrial sources of NDMA also were discharged during the weekend. NDMA concentrations remained at background levels (80 to 90 ng/L) throughout the week with slightly higher concentrations (190 ng/L) detected in the Monday sample. Results indicate that periodic industrial discharges have the potential to increase average daily NDMA concentrations by a factor of 2 to 4, resulting in NDMA concentrations as high as 400 ng/L.

The trend in NDMA precursors was similar, showing that twice as many NDMA precursors were discharged to SJ/SC WPCP during the middle of the week than on the weekend (Fig. 3-3). NDMA precursor concentrations were fairly constant throughout the week at OCSD Plant 1, ranging from 4500 to 5500 ng/L (data included in Table 3-3).

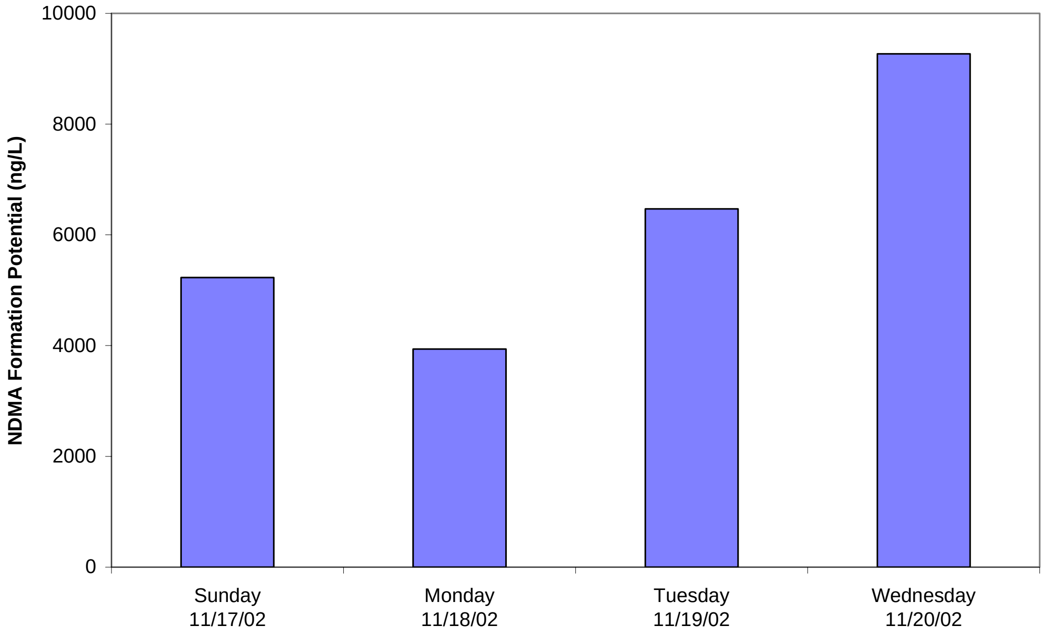


Figure 3-3. Weekly variation in NDMA precursors in SJ/SC WPCP primary effluent.

These findings are consistent with the project team's hypothesis of periodic batch industrial discharges of NDMA and NDMA precursors to the sewer. Industrial discharges can increase the average daily NDMA concentration by a factor of 2 to 4, resulting in up to 400 ng/L of NDMA. Average daily NDMA precursor concentrations increased by a factor of 2, up to 9000 ng/L. As illustrated by OCSD, the average daily variation can be comprised of shorter duration, highly concentrated NDMA and NDMA precursor discharges (e.g., up to 2000 ng/L of NDMA was observed over a 4-h period) (OCSD, 2002).

3.3.2 Impact of Industrial Activity on NDMA and NDMA Precursor Concentrations

Figure 3-4 shows the average NDMA levels detected in influent or primary effluent at each treatment plant. Error bars denote the maximum and minimum concentrations of NDMA detected.

The data show a distinct trend of increasing average NDMA concentrations and a wider range of observed concentrations at treatment facilities located in industrial areas compared with those in residential areas. The only exception to the general trend is OCSD Plant 2, which was only sampled twice. NDMA concentrations typically ranged from 50 to 100 ng/L in residential areas and did not exceed 200 ng/L. In contrast, treatment facilities in industrial areas with greater than 10% industrial contribution averaged approximately 150 ng/L of NDMA. In these industrial areas, some influent and primary effluent samples contained as much as 790 ng/L over a 24-h period.

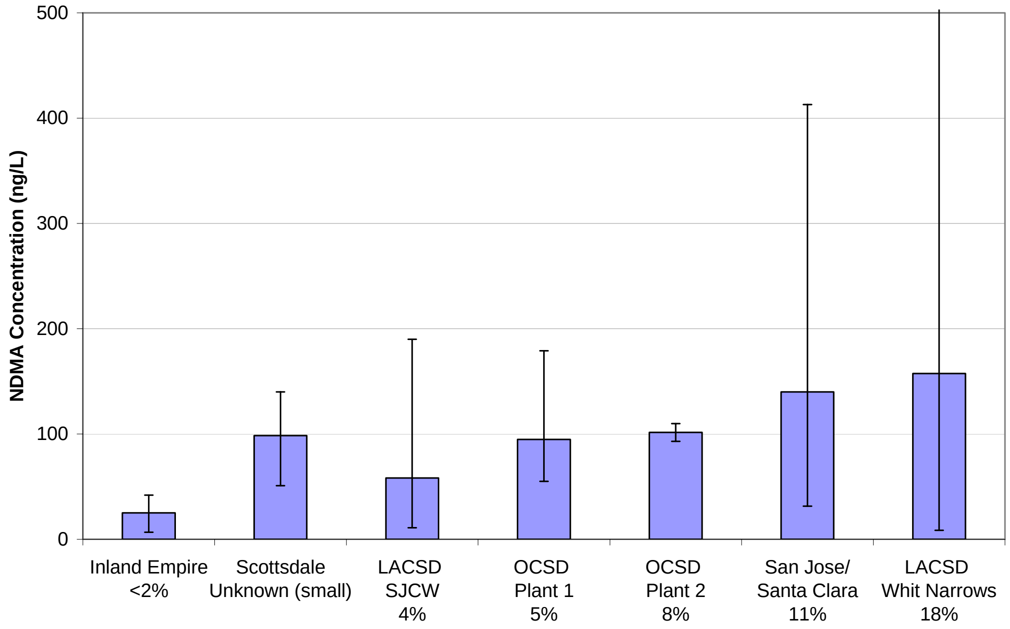


Figure 3-4. Impact of industrial activity in the wastewater service area on influent NDMA concentration.

NDMA precursors followed a similar trend, with a wider range of observed concentrations at treatment facilities in industrial areas. (An exception is the SJCW facility, in which polymers added during the treatment process were found to be NDMA precursors, as discussed in Chapter 4, Section 4.3.3.) Average NDMA precursor concentrations are plotted in Figure 3-5, with error bars denoting the maximum and minimum concentrations observed. Higher NDMA precursor concentrations were detected at facilities with greater industrial wastewater contributions.

In contrast, DMA concentrations were fairly constant among treatment plants regardless of industrial activity, ranging from 60 to 120 μg/L (Fig. 3-6). Concentrations at Scottsdale were slightly lower, ranging from 40 to 50 μg/L.

DMA concentrations did not vary significantly with industrial contributions, since DMA is primarily a component of domestic wastewater. These results suggest that DMA is not increasing substantially as a result of industrial activities. Other organic nitrogen compounds not yet identified may be contributing to the increase in NDMA precursors in industrial areas.

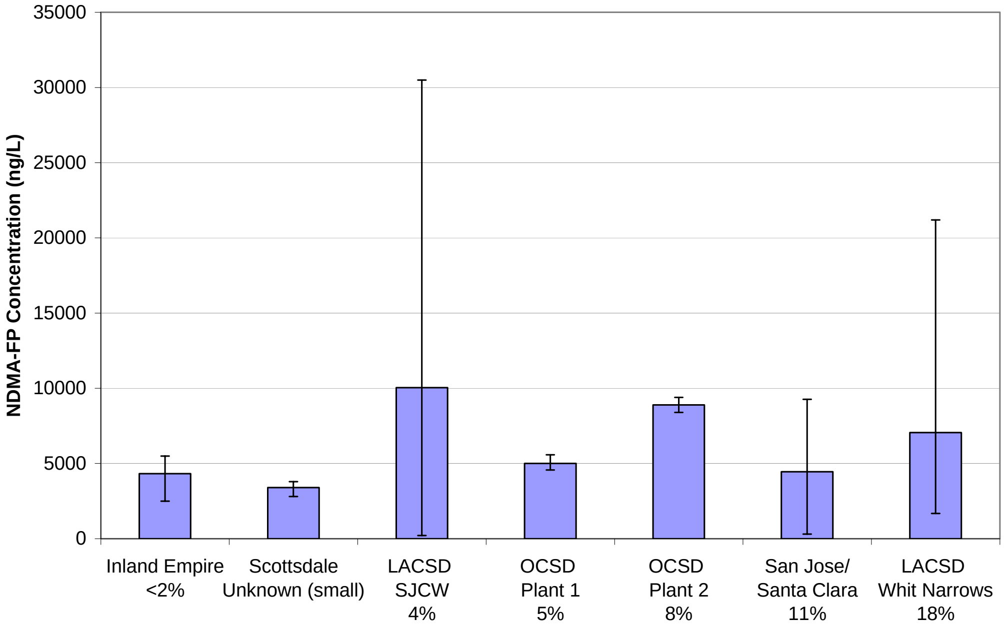


Figure 3-5. Impact of industrial activity on influent NDMA precursor concentration.

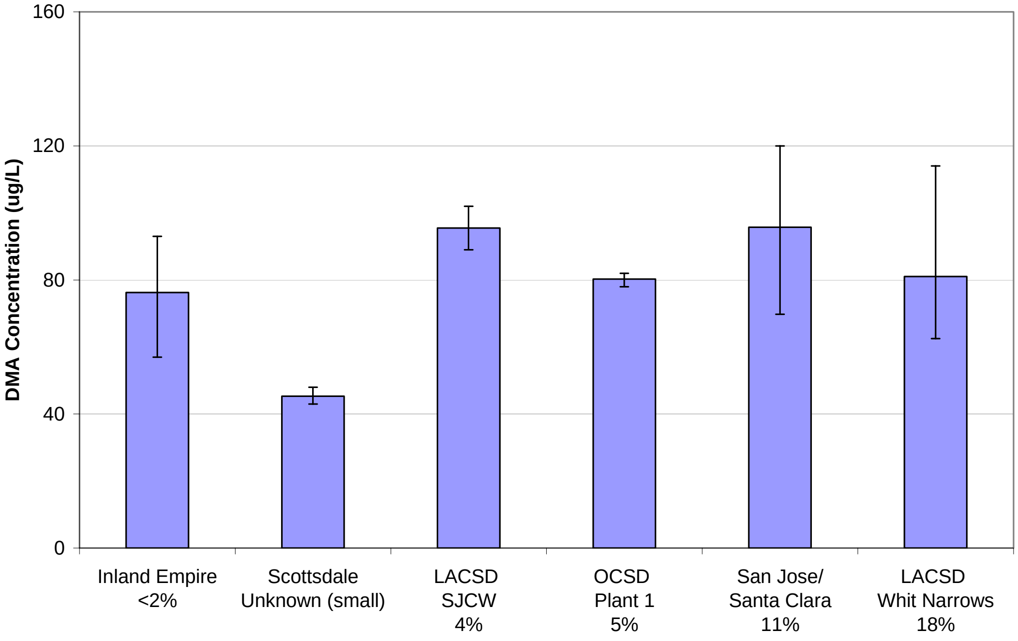


Figure 3-6. Impact of industrial activity on influent DMA concentration.

3.3.3 Industrial Sources of NDMA and NDMA Precursors

As described in the previous section, NDMA and NDMA precursor concentrations in raw sewage are correlated with the percentage of wastewater from industries within a treatment facility's collection area. To confirm NDMA discharges from specific industrial processes, the project team collected 12-h composite samples of wastewater discharged from two metal plating industries in the OCSD collection area. One metal plating company used dimethyldithiocarbamate (DTC) for metal chelation during industrial waste pretreatment. DTC has been implicated in previous OCSD studies as an NDMA precursor (OCSD, 2002). A sample was also collected from a trunkline containing primarily domestic wastewater. All samples were analyzed for NDMA and NDMA precursors at OCSD laboratories. DMA samples were collected and analyzed at UC Berkeley. Results are presented in Table 3-4.

Table 3-4. Summary of NDMA and NDMA Precursors Measured in Residential and Industrial Sources

Location	Location Description	NDMA, ng/L	NDMA Precursors, ng/L	DMA, µg/L
Domestic Wastewater	Trunkline	40	8150	77
Cirtech Industry (Non-DTC Process)	Industrial wastewater	29	1570	7
Pioneer Circuit (DTC Process)	Industrial wastewater	4230	82,500	1242

Other industries that potentially use DTC in their waste pretreatment process include printed circuit board manufacturers (OCSD, 2002). Circuit board plating shops adopted the use of dithiocarbamates in the late 1990s, using products advertised as Metal Grabber and WT-140. These products offered an economic advantage over traditional ferrous sulfide treatment chemistry. According to a wastewater treatment chemical vendor, DTC chemicals are not currently used as widely because more-effective, less-toxic chemicals are available (Wentz, personal communication). Options include sulfur-based polymers, such as Thio-Red (also known as WT-676), which is not as toxic as DTC yet effectively precipitates metals as stable thiocarbonates and sulfides. Calcium polysulfide, also known as lime-sulfur or WT-007, is also widely used. While calcium polysulfide is not as effective as DTC-based compounds for metal chelation, it is cheaper and more widely available. Because the use of DTC-based products is declining, these products are not likely to be important sources of NDMA entering wastewater treatment plants nationwide. Regionally, however, DTC-based compounds may be a significant source of NDMA entering a wastewater treatment facility. Utilities who are interested in assessing the use of DTC-based compounds in their collection area would need to collect or rely on regional surveys or estimates of DTC products used by local industries.

As previously demonstrated by the OCSD Source Control Division, carpet dyeing facilities are another potential source of NDMA. However, the chemical structures of the dyes responsible for NDMA formation have not yet been studied (OCSD, 2002).

3.3.4 Domestic Sources of NDMA and NDMA Precursors

The most common source of NDMA and NDMA precursors is domestic sewage, which contains DMA and other organic nitrogen compounds (Mitch and Sedlak, 2004). NDMA was detected in influent wastewater at each of the six treatment plants sampled in this study at levels ranging from 10 to 130 ng/L (as shown above in Table 3-2).

DTC-based fumigants can be applied directly to sewers in residential and industrial areas to control tree root growth. Examples of commercially available DTC-based herbicides include Sanifoam Vaporooter II (Airrigation), SeweRout (Florida Petrochemicals, Inc.), and Rout (Florida Petrochemicals, Inc.). These products contain between 15 and 30% methyldithiocarbamate (also known as metam sodium) when sold in concentrated form (Pesticide Action Network, 2005).

To investigate the NDMA formation potential of root control activities using DTC-based fumigants, the OCSD Source Control Division applied Sanifoam Vaporooter II to a sewer trunkline in a neighborhood. A 12-h composite sample was collected prior to product application, and a grab sample was collected during product application. As shown in Table 3-5, NDMA concentrations were elevated by 2 orders of magnitude and NDMA precursors increased by 1 order of magnitude during herbicide application.

Table 3-5. Summary of NDMA and NDMA Precursors Measured in Domestic Wastewater

SampleTiming	Sample Description	NDMA, ng/L	NDMA Precursors, ng/L	DMA, µg/L
Prior to herbicide application	12-h composite	40	8140	77
During herbicide application	Grab sample	2400	89,000	51

Dimethylamine concentrations did not increase during product application, suggesting that either the active ingredient, monomethyldithiocarbamate, or some other byproduct is the main NDMA precursor, not dimethylamine.

Assuming that application instructions are followed, a downstream wastewater treatment plant could be impacted by elevated NDMA concentrations of 50 to 100 ng/L over a 1- to 2-h period. The prevalence of DTC application to sewers for root control is not known. A query of the California Department of Pesticide Regulation's Pesticide Information Portal (CalPIP) data server returned no results for metam sodium application to sewage systems (septic tanks, sewers, etc.) in the year 2002, suggesting that applications are not regularly reported (CalPIP, 2005).

3.4 CONCLUSIONS

Both domestic and industrial activities contribute to NDMA and NDMA precursors entering wastewater treatment plants. Residential sources of NDMA include DMA and other naturally occurring organic nitrogen precursors as well as DTC-based herbicides used for tree root control in the wastewater collection system. Average daily NDMA concentrations in residential areas typically range from 50 to 100 ng/L. Concentrations did not exceed 200 ng/L at the treatment facilities located in residential areas that were included in this study. NDMA precursor concentrations ranged from 2500 to 5500 ng/L.

Industrial sources of NDMA and NDMA precursors include metal plating industries and printed circuit board manufacturing shops that use DTC in waste pretreatment processes in order to comply with metal discharge requirements. NDMA concentrations in industrial areas averaged approximately 150 ng/L, with a maximum daily average concentration of 790 ng/L. Point sources (root control treatments with metam sodium and DTC-containing metal treatment systems) accounted for approximately half of the identified sources of NDMA entering OCSD’s Plant 1 wastewater treatment plant, with the other half originating in domestic sewage (OCSD, 2002). NDMA precursor concentrations were elevated in industrial areas, with concentrations ranging from 1680 to 18,000 ng/L.

Restricting specific industrial practices that are major sources of NDMA may be effective in reducing NDMA effluent concentrations, especially if NDMA is not well-removed during wastewater treatment (as discussed in Chapter 4). However, the data suggest that while source control activities may reduce NDMA and NDMA precursor concentrations, the remaining NDMA concentrations are still high enough to warrant treatment. Regardless of industrial activity, NDMA precursor concentrations are high enough to form NDMA concentrations that exceed the California notification level upon chlorine disinfection, with or without nitrification.

Source control actions focused on root control applications and metal treatment systems may help to eliminate the occasional pulses of NDMA observed in treatment plants. Elimination of NDMA pulses is desirable at plants where UV treatment is used for NDMA removal, because the removal efficiency (i.e., percent removed) is normally constant (i.e., increases in influent concentrations would result in higher effluent concentrations). In the future, as facilities divert more treated wastewater to advanced treatment and groundwater reuse, it will become more important for them to limit sources of NDMA and NDMA precursors to wastewater treatment facilities.

CHAPTER 4

FATE OF NDMA AND NDMA PRECURSORS DURING CONVENTIONAL WASTEWATER TREATMENT

4.1 BACKGROUND

Little data have been published on the efficacy of conventional municipal wastewater treatment (i.e., primary settling, activated sludge, media filtration) for removing NDMA and NDMA precursors. The extent of NDMA and NDMA precursor removal during conventional wastewater treatment is important for two reasons. First, if NDMA can be sufficiently removed during conventional wastewater treatment, utilities will not need to consider source control measures (described in Chapter 3). Second, if a significant fraction of NDMA can be removed by adjusting conventional treatment practices (such as improving nitrification-denitrification or increasing the retention time within the plant), wastewater utilities may be able to make modest changes to their existing conventional treatment systems to meet NDMA effluent requirements instead of installing reverse osmosis and/or UV treatment systems.

As part of Task 3, Formation and Removal of NDMA and NDMA Precursors during Conventional Wastewater Treatment, the project team developed research objectives to determine the following:

- Typical NDMA and NDMA precursor concentrations in chlorinated secondary effluent.
- Typical removal rates of NDMA and NDMA precursors during primary and secondary wastewater treatment.
- The reliability of NDMA and NDMA precursor removal by conventional activated sludge treatment at a given facility.
- The impact of influent water quality or plant operating conditions on NDMA and NDMA precursor removal rates.
- The ability to predict NDMA and NDMA precursor removal at a given facility using influent water quality data and operational parameters for treatment processes.
- The potential for utilities to control effluent NDMA levels without installing advanced treatment processes, such as reverse osmosis or UV treatment.
- The potential for utilities to reduce NDMA in wastewater effluents by restricting industrial discharges of NDMA and NDMA precursors.

4.2 METHODS

The project team collected 24-h composite samples from seven different wastewater treatment facilities. Design characteristics of the facilities included in the study are shown in Table 4-1. Each facility used the activated sludge process for secondary treatment. Five out of the seven facilities employed at least partial nitrification-denitrification following activated sludge treatment.

Table 4-1. Summary of Wastewater Characteristics and Processes at Wastewater Treatment Plants (Sedlak et al., 2005)

Location	Design Flow, m^3/s (MGD)	% Industrial Contribution	Secondary Treatment	Advanced Treatment	Disinfection
Inland Empire RP-1	1.9 (44)	<2	Activated sludge	NDN	HOCl
Whittier Narrows	0.66 (15)	18	Activated sludge	NDN	HOCl
OCSD Plant 1	2.5 (58)[b]	5	Activated sludge	None	HOCl
OCSD Plant 2	3.9 (90)[b]	8	O_2-activated sludge	None	HOCl
San Jose Creek West	1.3 (30)	4	Activated sludge	None/NDN[c]	Cl_2
San Jose/Santa Clara	7.3 (167)	11	Activated sludge	NDN, filtration	HOCl
Scottsdale	0.69 (16)	Unknown[d]	Activated sludge	NDN	HOCl

Note: NDN, nitrification-denitrification.

[a] The Whittier Narrows and San Jose Creek West WWTPs were operated by the LACSD.

[b] Value represents the design flow for secondary treatment. The OCSD's Plant 1 WWTP has a design flow of 4.7 m^3/s for primary treatment, and the OCSD's Plant 2 WWTP has a design flow of 7.3 m^3/s for primary treatment. Primary effluent from both WWTPs was discharged through an ocean outfall.

[c] The San Jose Creek West WWTP was operated without nitrification-denitrification before June 2003.

[d] Estimates of the industrial contribution to the Scottsdale WWTP were unavailable. However, plant operators were unaware of large metal plating or printer circuit board manufacturing facilities in the service area.

Sample collection and analysis methods were described in Chapter 3; however, they are described here again for readers who have not referenced previous chapters. Samples were collected using refrigerated ISCO composite samplers equipped with Teflon-lined polypropylene containers. Samples were analyzed for NDMA and total NDMA precursors at either the OCSD or LACSD using continuous liquid-liquid extraction or liquid-liquid extraction followed by chemical ionization, isotope dilution, and GC/MS. The detection limit for NDMA in secondary effluent ranged from 1 to 10 ng/L. The detection limit in the more complex matrix of untreated wastewater and primary effluent ranged from 10 to 40 ng/L. NDMA precursors were determined using the NDMA precursor test. The test consisted of adding pH buffer and a large dose of monochloramine (140 mg/L as Cl_2) to the sample and allowing the reaction of monochloramine and organic precursors to go to completion over 5 to 10 days, forming NDMA and a variety of other products. The sample was then analyzed for NDMA. A more complete description of the analytical method has been provided by Mitch et al. (2003a).

Samples were analyzed for DMA at UC Berkeley using GC/MS/MS following derivatization with 4-methoxybenzenesulfonyl chloride (Mitch et al., 2003a). The detection limit for DMA was approximately 0.5 µg/L. Other water quality parameters, including ammonia, nitrate, nitrite, total suspended solids, alkalinity, total organic carbon, and dissolved organic carbon, were analyzed using standard methods (APHA, 1998) at either OCSD, LACSD, San Jose/Santa Clara, or the City of Scottsdale.

4.3 RESULTS AND DISCUSSION

4.3.1 NDMA Removal during Primary and Secondary Treatment

Primary treatment removed a negligible amount of NDMA. This was expected, since NDMA is highly water soluble and has a low affinity for sewage particles. The median concentrations of NDMA in wastewater influent and primary effluent were similar (88 ng/L in wastewater influent, 73 ng/L in primary effluent). As shown in Figure 4-1, concentrations of NDMA in wastewater influent and primary effluent samples were well-correlated (coefficient of correlation $r^2 = 0.95$) for all but two samples.

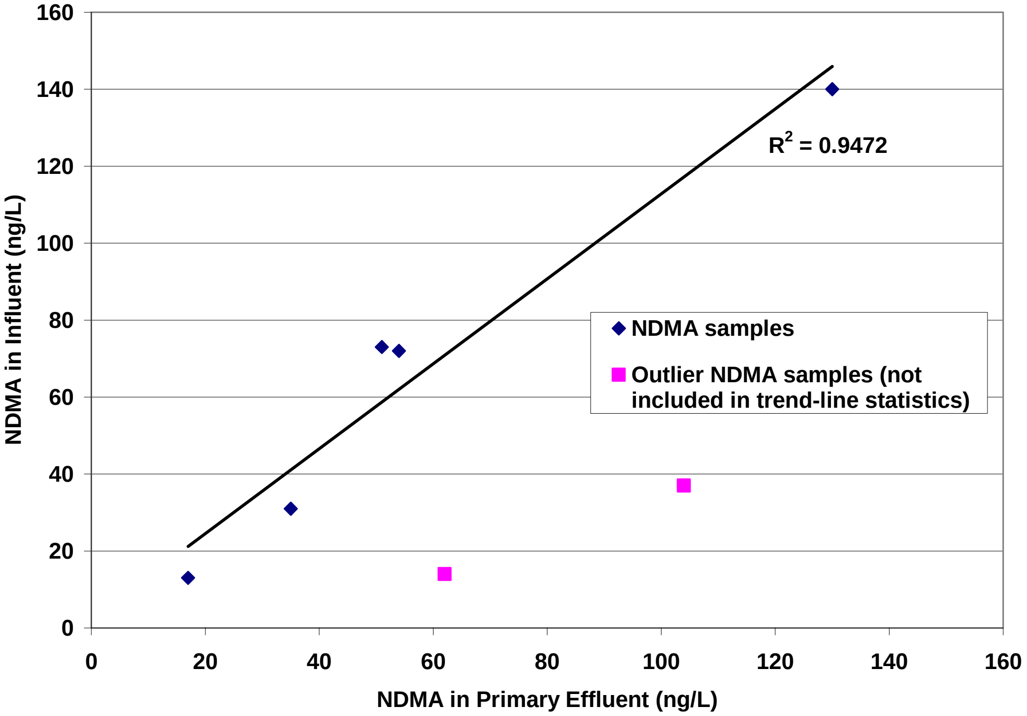


Figure 4-1. Summary of NDMA concentrations in influent and primary effluent.

The two samples that showed significant NDMA removal during primary treatment (65% to 77% removal) may be biased low due to the complex matrix of raw wastewater. One of the two samples was collected from LACSD's Whittier Narrows (WN) facility on Oct. 21, 2003. The other was collected from the SJ/SC WRCP on Sept. 17, 2003. Both samples were analyzed at the LACSD laboratory, where laboratory personnel have occasionally observed low recoveries in sewage influent samples. In general, NDMA concentrations in influent and primary effluent were approximately equivalent.

During secondary treatment, variable NDMA removal was observed from day to day at several facilities where sampling efforts were concentrated. For example, NDMA removal at LACSD Whittier Narrows ranged from 12% to 90%. An increase in NDMA during secondary treatment was observed on two days, as discussed in more detail in Section 4.3.3. At SJ/SC WPCP, NDMA removal varied from little or no removal to 75% removal (Fig. 4-2).

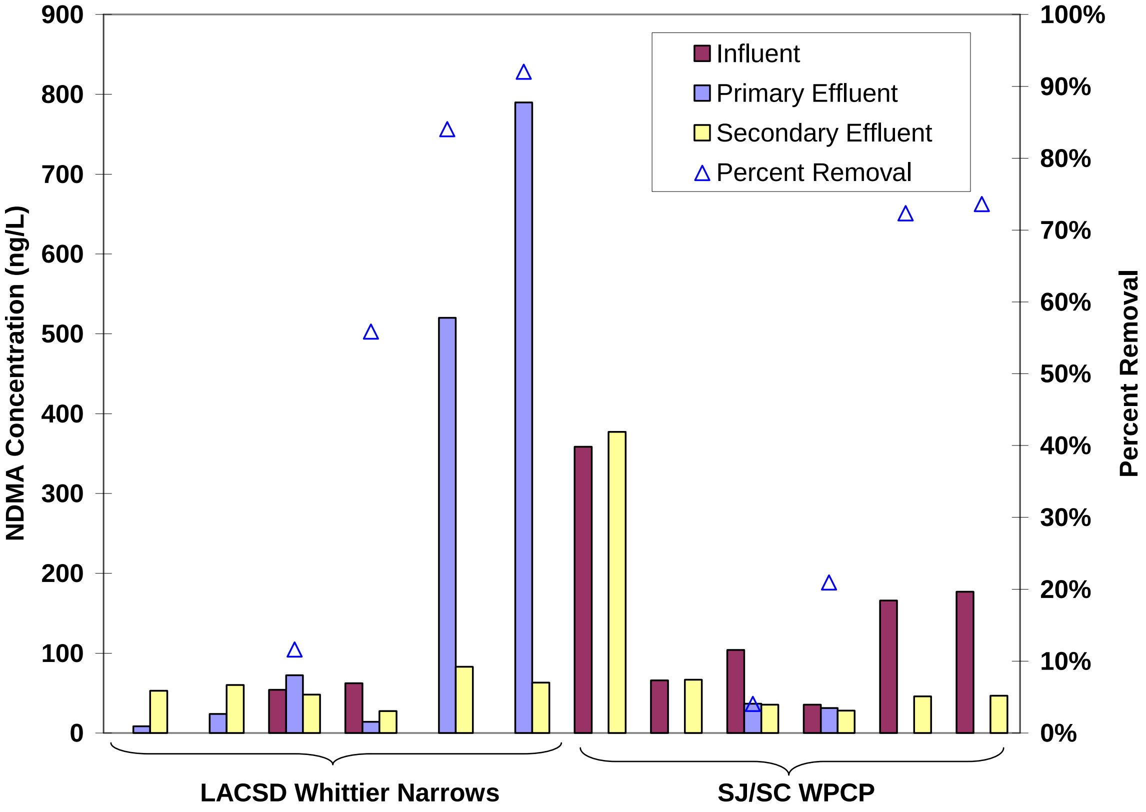


Figure 4-2. Variable NDMA removal during secondary treatment.

There was no obvious reason for the variability of NDMA removal at these facilities, such as plant upsets, changes in operating procedures, or variations in influent wastewater quality. Removal rates at other treatment plants were more consistent over time. Removal at OCSD Plant 1 was negligible (0% to 25%). NDMA removal rates ranged from 50% to 90% at OCSD Plant 2, Inland Empire Reclamation Plant 1, and City of Scottsdale Water Campus (Fig. 4-3).

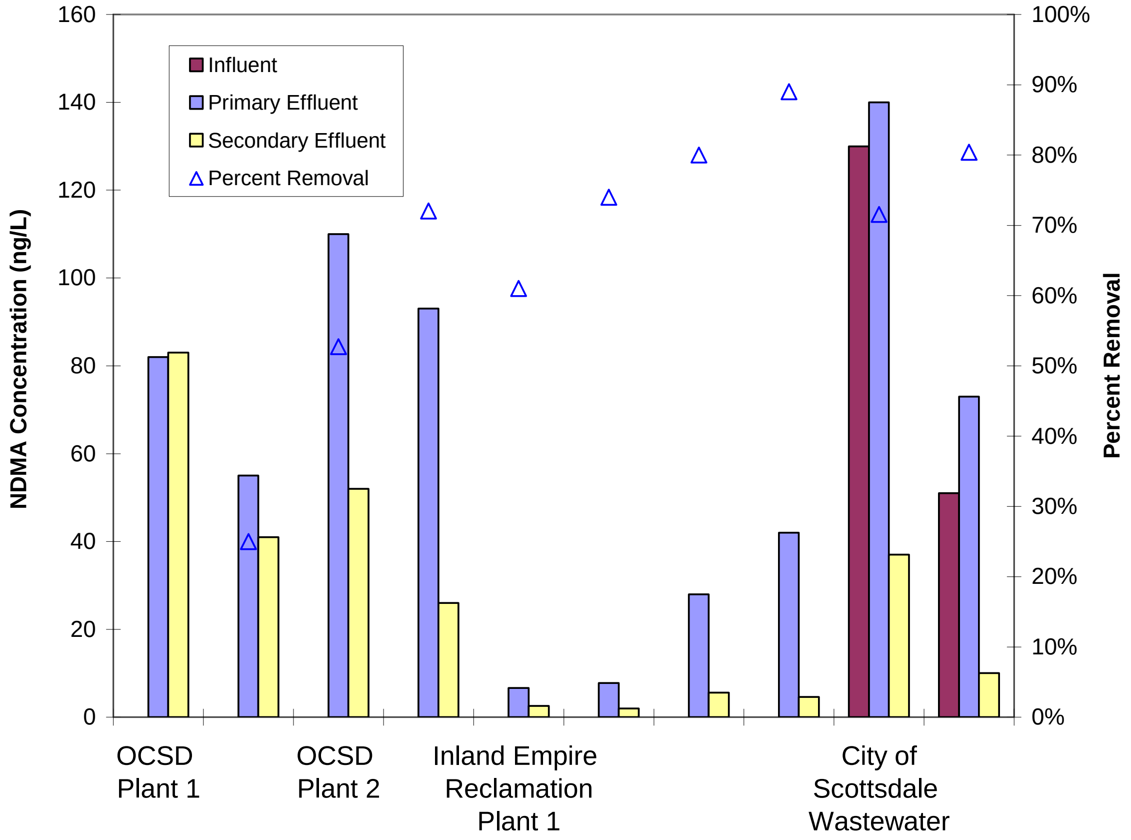


Figure 4-3. Range of NDMA removal during secondary treatment.

This study shows that NDMA removal is highly variable at a given treatment facility. There was wide variation in removal rates from day to day at facilities such as LACSD Whittier Narrows facility and SJ/SC WPCP. The reasons for the inconsistent removal of NDMA during conventional activated sludge is suggested as an objective for a follow-up study. For example, NDMA has been shown to biodegrade. There may be a correlation between the presence of particular microbial species or enzymes and NDMA removal during secondary treatment.

4.3.2 NDMA Precursor Removal during Primary and Secondary Treatment

Similar to NDMA, NDMA precursors were not well-removed during primary treatment. These results agree with previous studies of NDMA precursors which concluded that most NDMA precursors were low molecular weight, dissolved, organic nitrogen compounds, not particles (Mitch et al., 2004). In wastewater influent samples, the median concentration of total NDMA precursors was 4600 ng/L; in primary effluent samples, the median concentration of NDMA precursors was 3800 ng/L. A subset of NDMA precursor results (those collected concurrently from influent and primary effluent) are shown in Table 4-2. The results demonstrate that NDMA precursors were not well-removed during primary treatment.

Table 4-2. NDMA Precursor Removal during Primary Treatment

Facility	Start Date	Influent, ng/L	Primary, ng/L	% Removal
LACSD SJCW	11/20/2002	3351	2899	13
SJ/SC WPCP	9/17/2003	3190	3110	3
City of Scottsdale Water Campus	9/28/2003	3400	3800	–12
City of Scottsdale Water Campus	9/29/2003	2800	3600	–29
LACSD Whittier Narrows	10/21/2003	4330	3670	15

Note: Data exclude an anomalous sample result from SJ/SC WPCP (9/16/03) in which NDMA precursors in the influent were measured as 298 ng/L while NDMA precursors in the primary effluent were measured to be 4130 ng/L.

Unlike NDMA, NDMA precursors were well-removed during secondary treatment. Exceptions noted at the LACSD San Jose Creek West (SJCW) and WN facilities were explained by the addition of wastewater treatment polymers that acted as NDMA precursors. This is discussed in more detail in Section 4.4 and by Mitch and Sedlak (2004). Aside from these exceptions, removal rates in secondary treatment for NDMA precursors typically ranged from 60 to 90%, as shown in Figure 4-4. At SJ/SC WPCP, during the same days that variable NDMA removal was observed (0 to 75%), total NDMA precursors were consistently removed (65% to 85%). Total NDMA precursors in influent or primary effluent ranged from 2400 to 9400 ng/L, while total NDMA precursors in secondary effluent were considerably lower (659 to 2800 ng/L).

The removal of total NDMA precursors can be partially explained by the high removal rates of the known NDMA precursor DMA. Good removal of DMA was observed at all treatment plants, with removal rates typically ranging from 96 to 99% (Fig. 4-5). As with total NDMA precursors, the only exceptions were linked to polymer usage at the LACSD SJCW and WN facilities. The results are consistent with previous analyses of grab samples at wastewater treatment plants, which showed greater than 90% removal of DMA during secondary treatment (Mitch and Sedlak, 2004).

Assuming that DMA reacts to form NDMA during the NDMA precursor test with a molar yield of 2.6% (Mitch and Sedlak, 2004), typical removal rates of DMA during secondary treatment account for the removal of total NDMA precursors observed. Assuming a median DMA concentration of 79 µg/L in primary effluent and 95% DMA removal, approximately 3400 ng/L of total NDMA precursors would be removed during secondary treatment. This is similar to the actual decrease in concentrations of total NDMA precursors measured in this study, as shown in Figure 4-4.

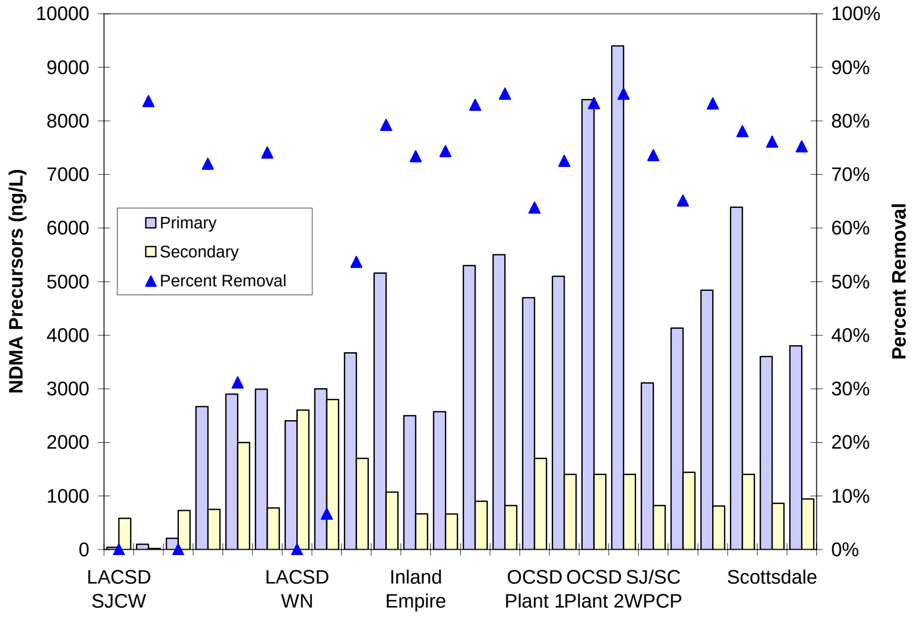


Figure 4-4. NDMA precursor removal during secondary treatment.

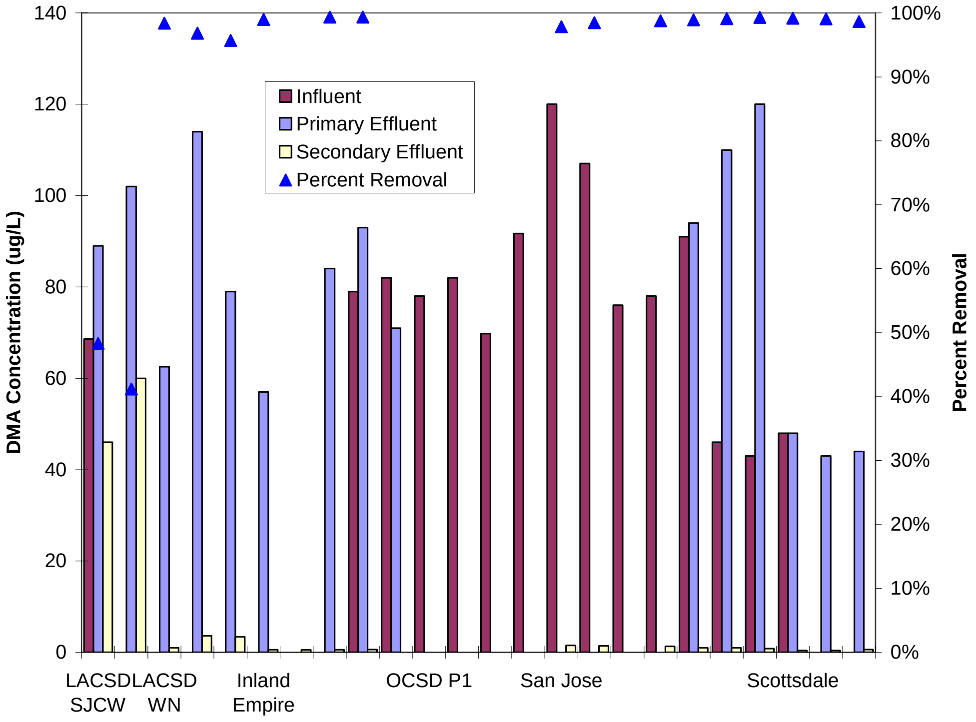


Figure 4-5. DMA removal during secondary treatment.

As shown in Table 4-3, other precursors are also removed during secondary treatment. At the LACSD Whittier Narrows treatment plant only 40 to 60% of total NDMA precursors removed during secondary treatment could be explained by DMA removal. Removal of NDMA precursors other than DMA was also noted at SJ/SC WPCP on several dates (Nov. 17 and Nov. 20, 2002).

Table 4-3. NDMA Precursor Removal Attributable to DMA

Facility	Date	DMA Removed, µg/L	Estimated NDMA Precursor Removal, ng/L	Actual NDMA Precursor Removal, ng/L	% Removal Attributable to DMA
Inland Empire	4/7/2003	56	2426	1833	132
	3/29/2004	83	3589	4680	77
	3/30/2004	92	3974	4400	90
LACSD WN	3/23/2004	110	4747	8145	58
	3/24/2004	76	3251	8765	37
SJ/SC WPCP	11/17/2002	68	2937	4546	65
	11/18/2002	90	3883	2920	133
	11/20/2002	106	4545	8464	54
	9/16/2003	109	4688	2690	174
	9/17/2003	119	5124	2290	224
Scottsdale	9/28/2003	48	2047	2860	72
	9/29/2003	43	1832	2740	67
MEDIAN		83	3420	2890	74
MAX		119	5124	8765	224
MIN		42	1806	1833	37

DMA is the most prevalent NDMA precursor in untreated wastewater. It accounts for most of the precursors detected in the wastewater prior to secondary treatment. However, the majority of the DMA is removed during secondary treatment. As a result, secondary effluent has fewer NDMA precursors, most of which consist of species other than DMA. Typically less than 5% (range, 2% to 11%) of NDMA precursors in secondary effluent can be attributed to DMA. The other 95% of total NDMA precursors remaining in secondary effluent are other unidentified organic nitrogen precursors.

DMA alone has the potential to form approximately 40 ng/L of NDMA when secondary effluent is chloraminated during the NDMA precursor test (the range observed in this study was from 17 to 155 ng/L). Other nitrogen precursors have the potential to form an additional 840 ng/L of NDMA after chloramination (the range observed in this study was from 180 to 3700 ng/L). The actual concentrations of NDMA formed in wastewater treatment plants will be considerably lower because lower doses of chloramines are used for effluent disinfection. Although levels of DMA remaining after secondary treatment have the potential to form

NDMA in excess of the California notification level of 10 ng/L, future research should focus on the identity and degradability of NDMA precursors that survive secondary treatment. If these compounds are biodegradable, increasing the retention time of an activated sludge process or providing favorable redox, pH, or nutrients would increase NDMA precursor removal during secondary treatment.

4.3.3 Unexpected Increase in NDMA Precursors during Conventional Treatment

During two days of sampling at the LACSD SJCW facility (March 23 and 24, 2004), both NDMA and NDMA precursor concentrations increased during secondary treatment. DMA removal rates were much lower than expected, approximately 41% and 48% (Table 4-4).

Table 4-4. Results from LACSD SJCW Facility during Polymer Recycling

Compound	Date	Primary Effluent, ng/L	Secondary Effluent, ng/L	% Removal
NDMA	3/23/04	24, 33	110, 70	–358 to –112
NDMA	3/24/04	33, 11	86, 81	–161 to –636
NDMA Precursors	3/23/04	1200, 20,300	27,100, 21,200	–2158 to –4
NDMA Precursors	3/24/04	5400, 30,500	28,900, 19,700	–435 to 35
DMA	3/23/04	89	46	48
DMA	3/24/04	102	60	41

Previous studies at LACSD wastewater treatment facilities, including the SJCW facility, identified wastewater treatment polymers as NDMA precursors (Neisess et al., 2003). The Mannich-type cationic polymers used at SJCW are polyacrylamide- or methyl amine-based, formulated with DMA and formaldehyde. Polymer is typically dosed at 0.5 to 1.5 mg/L prior to filtration to control foaming and improve settling (Neisess et al., 2003).

The increase in NDMA and NDMA precursors observed during secondary treatment may have been caused by recycling filter backwash water containing polymers. At the SJCW facility, the 14 filters were sequentially cycled on a 24-h backwash schedule. Backwash recovery water was recycled via mixing with primary effluent. The polymer may have persisted in filter backwash water, elevating the NDMA concentrations. Chlorine is routinely applied at this facility prior to filtration for disinfection and to control biological growth on the dual media filters (Neisess et al., 2003).

During the sampling event in March 2003, water from another treatment facility (San Jose Creek East facility) was diverted to the SJCW facility. Higher doses of polymer (1.7 mg/L) were needed to maintain filter effluent quality. As a result, NDMA and NDMA precursors increased during secondary treatment. DMA removal was much lower than usual due to higher DMA loading rates. Removal rates were similar to those reported by Hwang et al. (1994; 1995) of approximately 50% in conventional activated sludge treatment plants.

Polymers used for drinking water treatment have already been identified as NDMA precursors. For example, Najm et al. tested several types and doses of drinking water treatment polymers, including poly-DADMAC and polyacrylamide polymers, measuring the effect on DMA release and NDMA formation during chloramination (Najm et al., 2004). They found that all types of polymers contributed DMA to drinking water and elevated NDMA levels. These findings also were consistent with similar experiments reported by Mitch and Sedlak (2004) and studies of full-scale drinking water treatment plants where poly-DADMAC polymers were used (Wilczak et al., 2003).

Eliminating the use of dimethylamine-based polyacrylamide polymers will reduce NDMA concentrations. Other polymers have also been shown to produce less NDMA during chloramination {e.g., *N*,*N*,*N*-trimethyl-2-[(1-oxo-2-propenyl)oxy] ethanaminium-based polyacrylate cationic polymer, also known as an ADAMQUAT polymer} (Mitch and Sedlak, 2004). Based on the mixed results of NDMA removal during secondary treatment, it would be difficult to tell whether precursors were being added by looking at the NDMA results alone. However, the increase in total NDMA precursors during secondary treatment is a good indication that certain types of treatment polymers are being added within the plant.

4.3.4 Formation of NDMA during Chlorination

Regardless of polymer practices, there usually are enough NDMA precursors remaining after secondary treatment to form significant levels of NDMA when ammonia-containing secondary wastewater effluent is subjected to chlorine disinfection or when chloramines are used for disinfection of a nitrified effluent. Composite samples collected from LACSD’s Whittier Narrows facility between June 2002 and February 2004 showed NDMA increases ranging from 20 to 540 ng/L, with a median increase of 120 ng/L. Final effluent concentrations of NDMA ranged from 52 to 640 ng/L, with a median concentration of 164 ng/L (Fig. 4-6).

Approximately 1 mg/L of ammonia was present in chlorinated secondary effluent at the Whittier Narrows facility. In contrast, little production of NDMA was observed during chlorine disinfection of nitrified effluent (ammonia, <0.1 mg/L) at the SJ/SC WPCP facility between Sept. 16 and Sept. 18, 2003. NDMA concentrations in secondary effluent ranged from 30 to 36 ng/L, concentrations in filtered tertiary effluent ranged from 18 to 38 ng/L, and concentrations in chlorinated effluent were between 15 and 26 ng/L. These data were consistent with results from laboratory studies indicating that disinfection with free chlorine (i.e., HOCl) results in much less production of NDMA than disinfection with chlorine in the presence of ammonia (i.e., chloramines) (Mitch and Sedlak, 2004). These data suggest that removing ammonia is the simplest way to reduce NDMA formation during disinfection with chlorine and lower the NDMA concentration in wastewater effluent. The amount of chlorine added throughout the plant should be minimized in order to control NDMA formation.

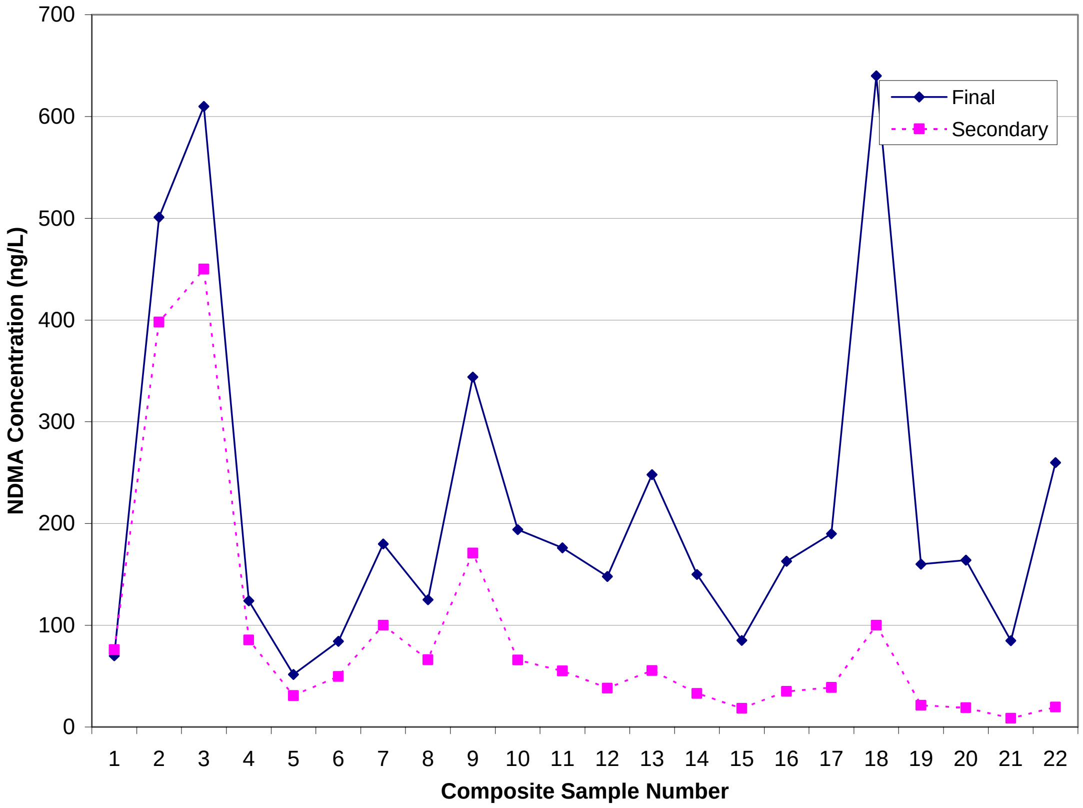


Figure 4-6. NDMA formation during chlorination of secondary effluent at LACSD Whittier Narrows facility in the presence of 1 mg/L of ammonia.

4.4 CONCLUSIONS

Conventional activated sludge treatment does not reliably remove NDMA. For example, removal at OCSD Plant 1 was negligible (0% to 25%), while removal at three other treatment facilities was good (50% to 90%). At SJ/SC WPCP, NDMA removal varied from little or no removal to 75% removal. In addition, utilities can unintentionally increase NDMA concentrations by introducing Mannich-type wastewater treatment polymers that act as NDMA precursors. NDMA also forms during chlorine disinfection of secondary effluent, especially in the presence of ammonia.

Concentrations of NDMA in secondary effluent prior to disinfection frequently exceed the California notification level of 10 ng/L. NDMA concentrations in 17 of the 21 secondary wastewater effluent samples analyzed in this study exceeded 10 ng/L prior to disinfection, with a median concentration of 46 ng/L and a maximum concentration of 380 ng/L. Although secondary treatment removes the majority of NDMA precursors (removal rate, 60% to 90%), including DMA (removal rate, >95%), relatively high concentrations of NDMA precursors remain in the treated water. Even if treated secondary effluent were subjected to UV treatment, destroying NDMA, the remaining NDMA precursors (659 ng/L to 2800 ng/L) could form NDMA in excess of the California notification level. This could occur if the UV-treated water were chloraminated at a later stage in the treatment process (e.g., in a distribution system for a nonpotable water reuse system) or if the wastewater effluent were discharged to a surface water that later served as a drinking water source.

To control NDMA levels in secondary effluent, utilities have several options: source control (i.e., limiting the amount of NDMA and precursors discharged to the wastewater treatment plant from known sources), improving NDMA and precursor removal during secondary treatment, and decreasing NDMA formation within the plant by changing polymer use and/or chlorination practices. Installation of advanced treatment systems (e.g., microfiltration and reverse osmosis) also might be appropriate when indirect potable reuse occurs.

Utilities with low or inconsistent NDMA removal rates (0–25%) could potentially benefit the most from source control efforts. For these facilities, a reduction of 40 ng/L in influent NDMA concentrations translates into 30 or 40 ng/L reduction in secondary effluent. Source control efforts are not as effective if NDMA is reliably removed during secondary treatment. For example, at treatment plants with consistently high NDMA removal (~75%), a reduction of 40 ng/L of NDMA in untreated wastewater would only result in a 10-ng/L reduction in secondary effluent. Similarly, source control efforts may reduce total NDMA precursors in wastewater influent but will have a minor impact on NDMA precursor concentrations in treated secondary effluent, since NDMA precursors are well-removed during secondary treatment.

Further research is necessary to determine how to improve NDMA removal rates during secondary treatment. Research is needed to determine the removal mechanism and whether or not optimization of the removal process is a viable control strategy for utilities. Because the most likely mechanism through which NDMA is removed during secondary treatment is biotransformation, studies aimed at identifying the organisms responsible for NDMA biotransformation and the conditions that are most conducive to NDMA biotransformation would be especially relevant.

Utilities concerned with NDMA should consider using an alternative to Mannich-type polymers or rerouting filter backwash after using these polymers instead of recycling the backwash water containing NDMA precursors through the plant. It may also be possible for utilities to reduce the chlorine dose applied during disinfection or practice nitrification-denitrification to remove ammonia prior to chlorine addition. This would greatly reduce the amount of NDMA formed during disinfection with chlorine. Alternative disinfectant practices, such as preforming monochloramines, may also reduce NDMA formation, as discussed in Chapter 5.

CHAPTER 5

REMOVAL OF NDMA AND NDMA PRECURSORS DURING ADVANCED WASTEWATER TREATMENT

5.1 BACKGROUND

5.1.1 Introduction

In order to meet water quality requirements for indirect potable reuse applications, many wastewater utilities have added advanced treatment processes following secondary treatment, such as nitrification-denitrification, MF, RO, and/or UV treatment. The performance of these advanced wastewater treatment systems for removing NDMA and NDMA precursors is not well-documented in the published literature. However, concerns with NDMA in the water produced by these systems has led to extensive scrutiny of system performance in California and, in some cases, to the installation of UV treatment systems for NDMA removal (see Mitch et al., 2003b for a review).

Few data are readily available on the fate of NDMA precursors during advanced treatment. Mitch et al. (2004) presented a brief discussion of NDMA precursor removal during MF and RO but did not conduct detailed studies on NDMA formation and removal in advanced wastewater treatment systems. Recently, more literature has become available on various aspects of UV treatment for NDMA, including UV modeling (Sharpless et al., 2003), use of pulsed UV (Liang et al., 2003), and advanced oxidation of NDMA (Mezyk et al., 2004). Interest in NDMA and NDMA precursor removal during advanced treatment is still fairly recent (i.e., within the last five years). Much of the information has been developed by treatment system vendors and wastewater utilities that are conducting NDMA monitoring and have advanced treatment processes in place.

5.1.2 Objectives

To investigate the removal and destruction of NDMA and NDMA precursors during advanced treatment (Task 4), the project team developed the following research objectives:

- Document the typical profile of NDMA and NDMA precursor concentrations at various points throughout the treatment plant to assess variability over time and among different utilities.
- Determine percent removal of NDMA and NDMA precursors in MF and RO units.
- Determine whether final effluent NDMA concentrations are typically below or within the range of advisory levels (~10 ng/L) after advanced treatment.
- Identify ways to improve NDMA removal or destruction in order to meet final effluent requirements consistently.
- Assess strategies to control NDMA formation by altering chlorination conditions prior to or during advanced treatment.

5.2 MATERIALS AND METHODS

5.2.1 Studies Performed

A laboratory study was conducted to test the hypothesis that preformed monochloramines reduced NDMA formation compared with in situ formation of monochloramines during advanced wastewater treatment. The project team set up and operated a pilot-scale MF unit to repeat the laboratory study at a larger scale without impacting full-scale facility operations and to also evaluate the importance of pH on NDMA formation kinetics. In addition, the project team also conducted sampling at three full-scale advanced wastewater treatment facilities with treatment trains consisting of MF-RO and/or UV to evaluate NDMA and NDMA precursor removal.

5.2.1.1 Laboratory Study of Preformed Monochloramines

A 24-h composite sample of wastewater effluent was collected prior to MF from the West Basin Municipal Water District (WBMWD) Water Recycling Plant. The sample was shipped to UC Berkeley for laboratory experiments, where it was divided into three portions. A high concentration of preformed monochloramines (~28 mg/L of chlorine premixed with ammonia) was added to the first portion. A similar concentration of free chlorine in the form of sodium hypochlorite was added to the second portion. The wastewater sample already contained enough ammonia (~39 mg/L) to form chloramines in situ in the second portion. The third portion served as a control. After 0.5 and 3.0 h, each of the treatments was analyzed for NDMA.

5.2.1.2 Pilot-Scale Study of pH and Preformed Monochloramines

The laboratory studies were repeated at pilot scale using a 15-gal/min (gpm) three-unit microfiltration system assembled at WBMWD. The unit was a skid-mounted, continuous flow model from Memcor with a membrane pore size of 0.2 µm (model 3M10V/C). The pilot unit was plumbed to receive WBMWD Water Recycling Plant influent (i.e., effluent from the Hyperion Wastewater Treatment Plant) that had been dosed with each disinfectant treatment tested in the study. Disinfectant such as chlorine or chloramine is typically added in full-scale MF facilities to control biological growth on the membranes. A 1000-L polyethylene mixing tank and feed pump were installed so that each disinfectant treatment could be added approximately 2 m upstream of the pilot unit. There was no mixer downstream of the application point.

Before sampling, the pilot unit was conditioned for three days by passing treated secondary effluent (WBMWD Water Recycling Plant influent) through the unit. During the 8 weeks of sampling, the unit operated continuously with one exception. For 15 days (July 15 to Aug. 1, 2004) the unit was shut down for cleaning. The unit was restarted after 1 h of conditioning.

During the experiment, five different disinfectant treatments were tested. The order of reagent addition to the mixing tank and the pH were varied in each test, as indicated by parentheses in the following list (i.e., reagents inside parentheses were mixed prior to addition to the other reagents):

1. Sodium hypochlorite + tap water
2. Ammonium chloride + [sodium hypochlorite + (pH 7.0 buffer + tap water)]
3. Sodium hypochlorite + [ammonium chloride + (pH 7.0 buffer + tap water)]
4. Ammonium chloride + [sodium hypochlorite + (pH 8.5 buffer + tap water)]
5. Sodium hypochlorite + [ammonium chloride + (pH 8.5 buffer + tap water)]

Treatment 1 consisted of 14% sodium hypochlorite diluted with tap water to make a stock solution of 4 meq/L of Cl_2. The pH of the tap water was 8.3. The volumetric ratio of disinfectant added to wastewater was approximately 30 to 1 in order to add 5 mg/L as Cl_2 to the wastewater stream. For treatments 2 through 5, tap water was first adjusted to pH 7.0 or to pH 8.5 using either hydrochloric acid or sodium hydroxide. Inorganic chloramines were formed by adding ammonium chloride and sodium hypochlorite in a Cl/N molar ratio of 0.77. Each reagent was paddle-mixed in the tank for approximately 5 min before the next reagent was added.

Samples were collected from the wastewater influent and MF effluent using flow-weighted 24-h refrigerated composite samplers. Disinfectant had contacted the wastewater for 4 minutes prior to sample collection downstream of the microfilters. Ascorbic acid (2.8 mM) was added to the composite sampling bottle to quench the disinfectant and stop NDMA formation upon sample collection. More details on sample collection, storage, and handling procedures are contained in Appendix B.

5.2.1.3 Studies Assessing NDMA and NDMA Precursor Removal Using MF, RO, and UV Treatment

Twenty-four-hour composite samples were collected from several locations at three advanced wastewater treatment plants: the OCWD Phase I Groundwater Replenishment System (formerly known as Water Factory 21), WBMWD Water Recycling Plant, and the City of Scottsdale, AZ, Water Campus. Samples from OCWD were collected from a pilot-scale treatment unit that was in operation at the time of sample collection; however, the treatment train and influent water quality were identical to the groundwater replenishment system that is currently operating at OCWD. Treatment plant characteristics are summarized in Table 5-1.

Table 5-1. Summary of Advanced Treatment Plant Characteristics

Facility Name	Average Flow Rate, MGD	Nitrification-Denitrification	Advanced Treatment Processes
OCWD Groundwater Replenishment System Pilot Facility	0.0072	No	MF, RO, UV
WBMWD Water Recycling Plant	30	No	MF, RO[a]
City of Scottsdale Water Campus	16	Yes	MF, RO

[a] Pilot-scale UV testing was complete and full-scale UV system construction was underway at the time of sample collection.

At OCWD, treated secondary effluent from Orange County Sanitation District Plant 1 passes through MF, RO, and UV before the water is blended with other sources and injected into four coastal aquifers. Injected water serves as a barrier to seawater intrusion. On average, more than half the injected water flows inland and augments potable water supplies (NRC, 1998). A schematic drawing of the treatment process is shown in Figure 5-1.

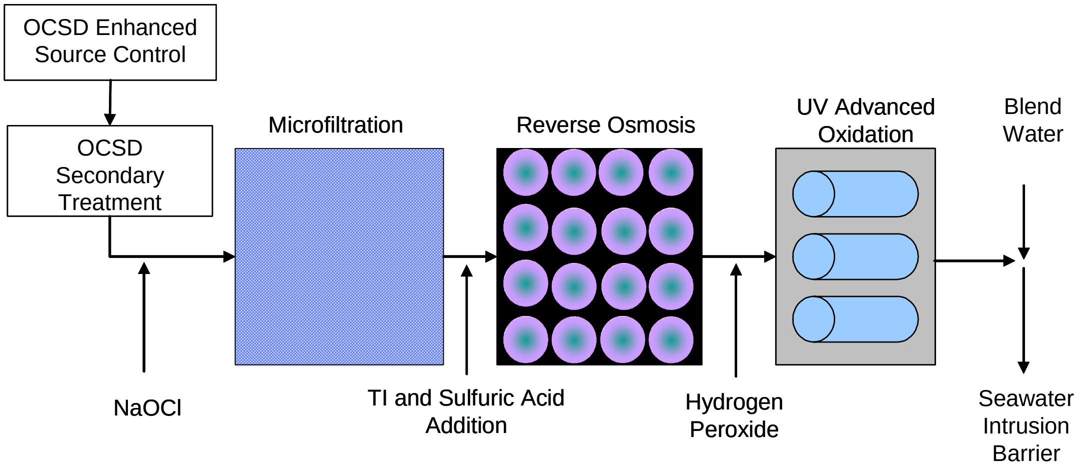


Figure 5-1. Process schematic of advanced treatment of the Phase I Groundwater Replenishment System, OCWD.

At the WBMWD Water Recycling Plant, secondary effluent from the City of Los Angeles Hyperion Treatment Plant is split into two streams for advanced treatment. One stream passes through lime treatment, media filtration, and RO, while the other stream passes through MF, thin-film composite membrane RO, and chlorination. The two streams are blended prior to aquifer injection as part of the West Coast Basin Barrier Project to prevent seawater intrusion. A schematic treatment process is shown in Figure 5-2.

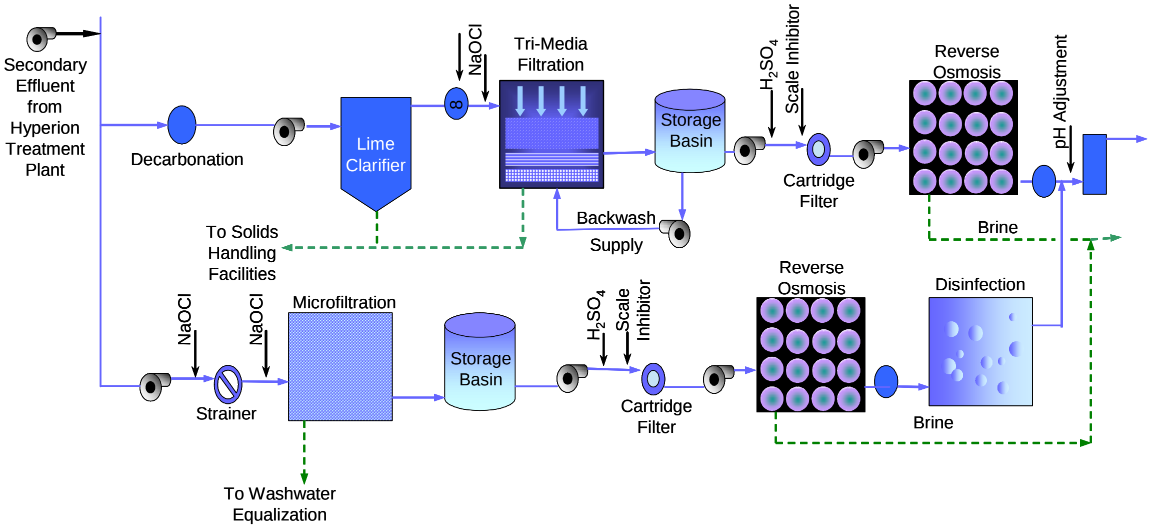


Figure 5-2. Process schematic of the WBMWD water recycling plant.

The City of Scottsdale Water Campus also employs MF and thin-film composite membrane RO prior to blending with surface water from the Central Arizona Project and reinjecting the water locally for aquifer replenishment. Schematic drawings of both conventional and advanced treatment processes at Scottsdale are shown in Figure 5-3.

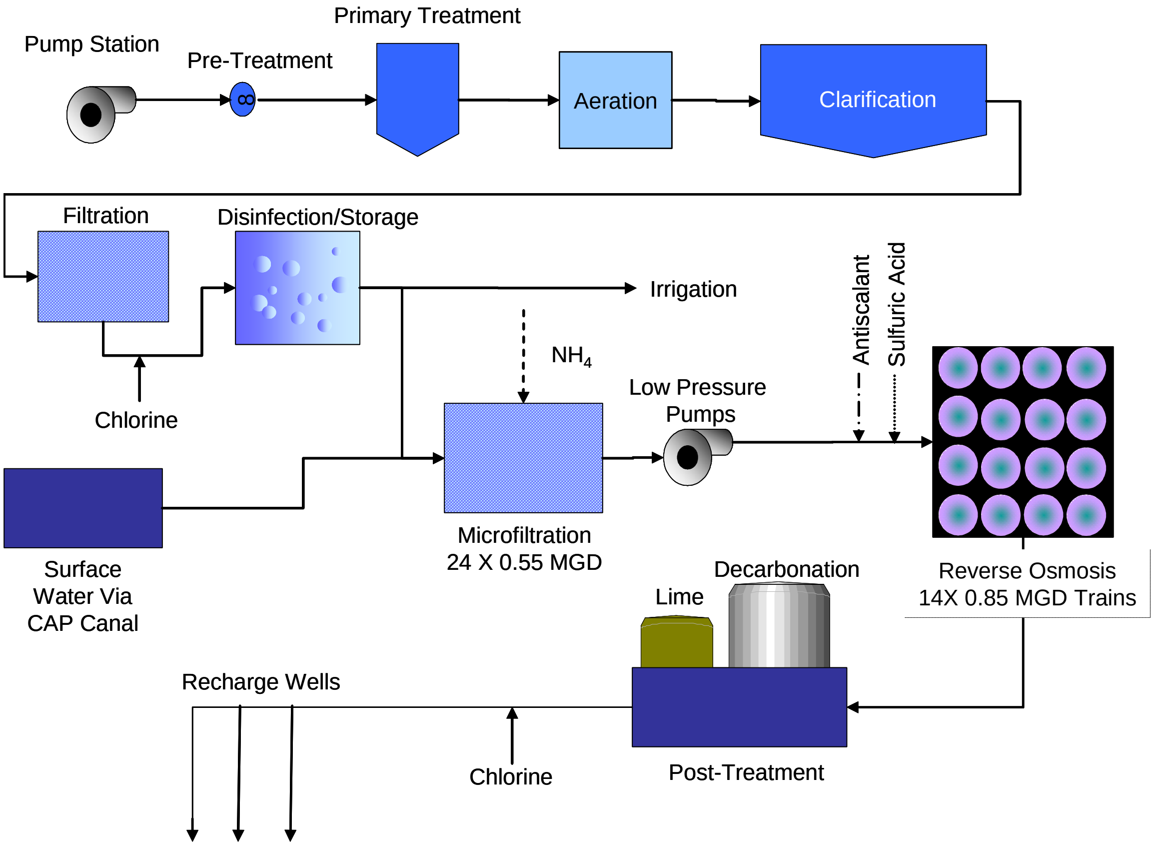


Figure 5-3. Process schematic for the City of Scottsdale Water Campus.

Twenty-four-hour composite samples were collected before and after MF, RO, and UV treatment at OCWD on seven different sampling events between December 2002 and May 2003. At Scottsdale, composite and/or grab samples were collected before and after MF and RO on May 3, 2004, and July 14, 2004. Details on sample collection protocols and QA/QC practices used in the study are provided in Appendix B.

Historical data collected prior to 2002 at West Basin were analyzed in conjunction with the data collected during this study. Grab samples were collected at West Basin before MF (73 samples), after MF (12 samples), before RO (20 samples), and after RO (51 samples). Data from WBMWD qualification testing of different UV treatment systems during September through November 2002 were also analyzed in conjunction with the study data.

5.2.2 Analytical Methods

Samples were analyzed for NDMA and total NDMA precursors at the OCWD laboratory using liquid-liquid extraction followed by chemical ionization and GC/MS/MS. Samples were analyzed for DMA at UC Berkeley using GC/MS/MS following derivitization with 4-methoxy-benzenesulfonyl chloride (Mitch et al., 2003a). Other water quality parameters, including conductivity, pH, nitrate, nitrite, ammonia, total organic carbon, and dissolved organic carbon, were analyzed using standard methods (APHA, 1998) at the City of Scottsdale, West Basin, and OCWD laboratories. More details on analytical protocols and analytical QA/QC measures used throughout this study are reported in Appendix B.

To standardize the stock disinfectant concentration during pilot-scale testing, total chlorine and free chlorine were measured daily using the *N*,*N*-diethyl-*p*-phenylenediamine (DPD) colorimetric method (APHA, 1998). Monochloramine and dichloramine were measured in the tank at the beginning and end of each 6-h experiment using UV spectrophotometry (Valentine et al., 1986). The total Cl[I] concentration showed good agreement with free chlorine measurements based on the DPD colorimetric method (8% ± 5% standard deviation).

5.3 RESULTS AND DISCUSSION

5.3.1 Laboratory Study of Preformed Monochloramines

Results from laboratory chlorination studies using WBMWD wastewater indicated that significant reduction of NDMA formation could be achieved by altering chloramination conditions and using premixed monochloramines. As shown in Figure 5-4, less NDMA formed in the laboratory sample containing preformed monochloramines.

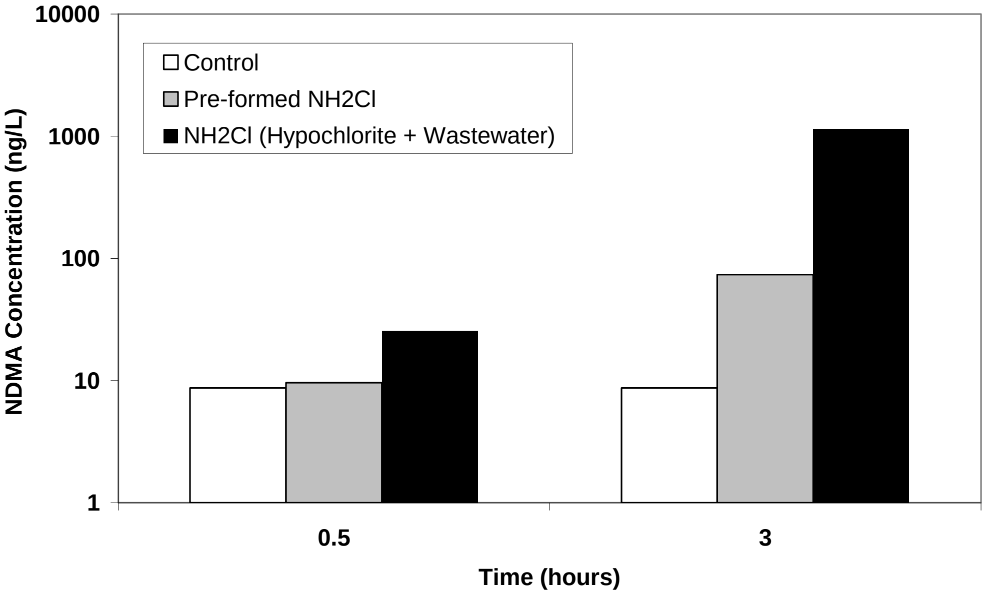


Figure 5-4. Comparison of NDMA formed in the laboratory under different disinfectant conditions [0.5 and 3 h at pH 6.8 with 0.4 mM oxidant (28 mg/L as Cl_2), 2.35 mM NH_3].

After 3 h at a high dose of disinfectant (28 mg/L of Cl_2), NDMA concentrations in the premixed batch reactor were approximately an order of magnitude lower than NDMA levels formed using the traditional disinfectant method (i.e., addition of free chlorine to wastewater containing ammonia). Since these preliminary results showed promise for utilities to reduce NDMA concentrations by changing chlorination practices, the project team proceeded with similar tests at pilot scale.

5.3.2 Pilot-Scale Study of pH and Preformed Monochloramines

In order to test the benefits of preforming monochloramines in a setting that was more representative of a full-scale facility, a pilot microfiltration unit was set up at West Basin MWD as described in Section 5.2.2. The pilot unit was also used to test whether or not an elevated pH had a significant effect on NDMA formation. Previous laboratory experiments at UC Berkeley have indicated that NDMA formation is a function of pH, with the maximum NDMA forming between pH 7 and 8 (Mitch and Sedlak, 2002a) (Fig. 5-5). At higher pH values, other byproducts are favored, such as formaldehyde dimethylhydrazone (Mitch and Sedlak, 2002a). At lower pH values, the NDMA formation reaction is slowed because only a fraction of the amine or ammonia is in the nonprotonated, active form (Mitch and Sedlak, 2002a).

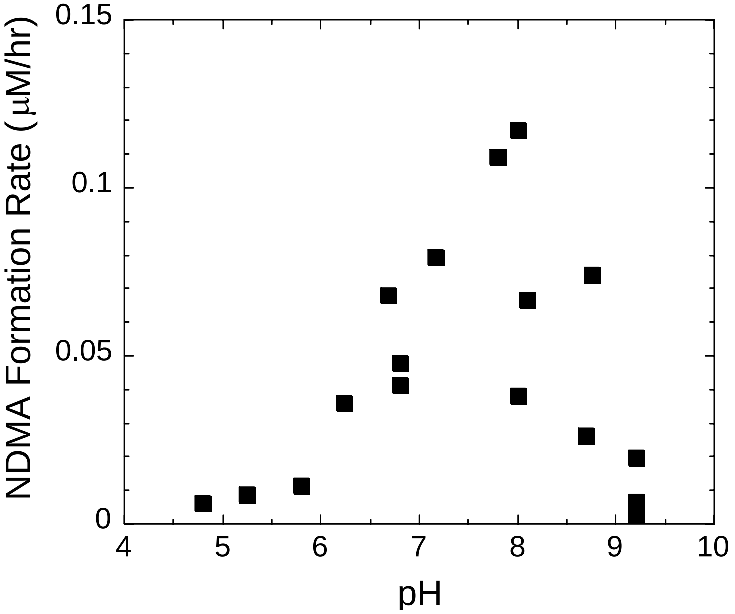


Figure 5-5. Effect of pH on the rate of formation of NDMA.

Initial conditions: 1 mM dimethylamine, 1 mM monochloramine (Mitch and Sedlak, 2002a).

The disinfectant conditions used for each treatment tested during the pilot-scale study are summarized in Table 5-2. Judging from the results presented in Figures 5-4 and 5-5, less NDMA was expected to form with treatments at elevated pH and with premixed monochloramines (treatment 5).

Table 5-2. Summary of Pilot Test MF Conditions at West Basin

Disinfection Treatment	Target pH	First Reagent Added	Second Reagent Added	Hypothesis
1	--	NaOCl	--	Control (tap water)
2	7.0	NH_4Cl	NaOCl	Highest NDMA formed
3	7.0	NaOCl	NH_4Cl	Low NDMA formed
4	8.5	NH_4Cl	NaOCl	High NDMA formed
5	8.5	NaOCl	NH_4Cl	Least NDMA formed

The results from the pilot-scale studies are shown in Figure 5-6.

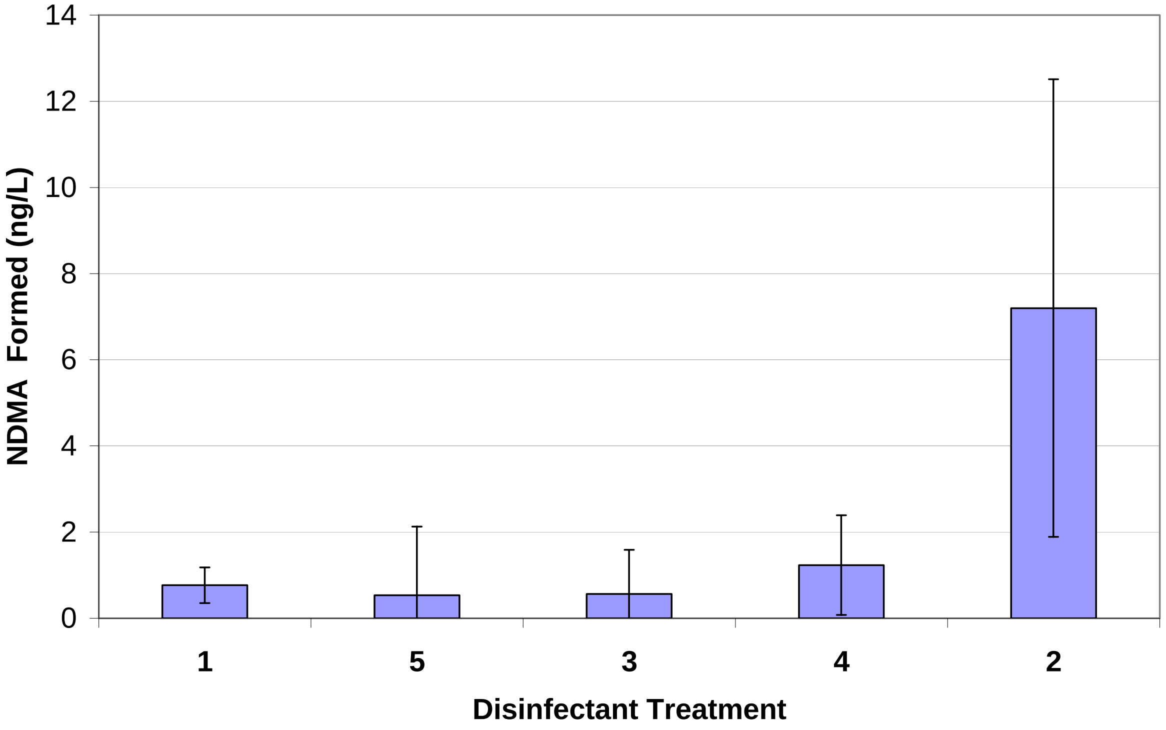


Figure 5-6. NDMA formation under different disinfection treatments (average formation over 3 days, with error bars denoting 1 standard deviation).

As expected, the most NDMA formation was observed in disinfectant treatments 2 and 4, in which monochloramines were not preformed but were formed in situ by adding chlorine to wastewater containing excess ammonia. The concentration of NDMA that formed across the MF unit was consistently less than 15 ng/L. However, in a full-scale system, more NDMA would have been formed because the full-scale system has a longer hydraulic residence time. The contact time in the pilot-scale unit was approximately 4 min, compared with 12 min at the full-scale facility at WBMWD. Assuming that the NDMA formation rate is constant over time (Schreiber and Mitch, 2005), approximately three times as much NDMA would have been formed under the conditions expected in the full-scale system.

Reduced NDMA formation in the presence of preformed monochloramines can be explained by the relative absence of dichloramine in the preformed chloramines solution. When dimethylamine reacts with dichloramine, the reaction rate has been shown to be much faster than when dimethylamine reacts with monochloramine, forming an order of magnitude more NDMA over time scales of several hours (Choi and Valentine, 2002; Mitch and Sedlak, 2002a; Schreiber and Mitch, 2005). When hypochlorite is added to wastewater that contains an excess of ammonia, dichloramine formation is favored locally at the point of hypochlorite addition due to the high Cl/N molar ratio prior to complete mixing (Fig. 5-7, top). Dichloramine then forms NDMA. When NDMA is preformed by adding hypochlorite first and ammonia second, the possibility of high concentrations of free chlorine in contact with ammonia is reduced. This decreases dichloramine formation (Fig. 5-7, bottom).

Figure 5-7 illustrates the concept of preforming monochloramines to reduce NDMA formation. At a full-scale facility, hypochlorite could be added to tap water at elevated pH. Downstream, ammonia could be added prior to running the water through a static mixer and then introducing it into the wastewater. However, a bulk storage tank was used in this study to simplify the experiment and to ensure that monochloramine was efficiently formed upstream of the microfilters.

Measurement of the concentrations of monochloramine and dichloramine species during the pilot study testing confirmed that more dichloramine was present when chloramines were formed in situ (treatments 2 and 4) than when the monochloramines were premixed (treatments 5 and 3) (Fig. 5-8).

As detailed by Mitch et al. (2005), the participation of dichloramine in NDMA formation requires that the time scale for dichloramine formation from chlorine and ammonia be comparable to the time scale for mixing. Although the mixing time in a chlorination system is extremely difficult to measure or model, the time scale for dichloramine formation was approximated to be 1.4 s, which is a reasonable time scale for mixing to occur (Mitch et al., 2005).

Utilities may be able to decrease the amount of NDMA that forms during MF by approximately 10 to 35 ng/L in full-scale facilities (assuming chlorination practices and residence times are similar to those at West Basin). Preventing NDMA formation has an added advantage in an MF-RO system, because the RO system removes NDMA precursors more effectively than NDMA, as described in the following section.

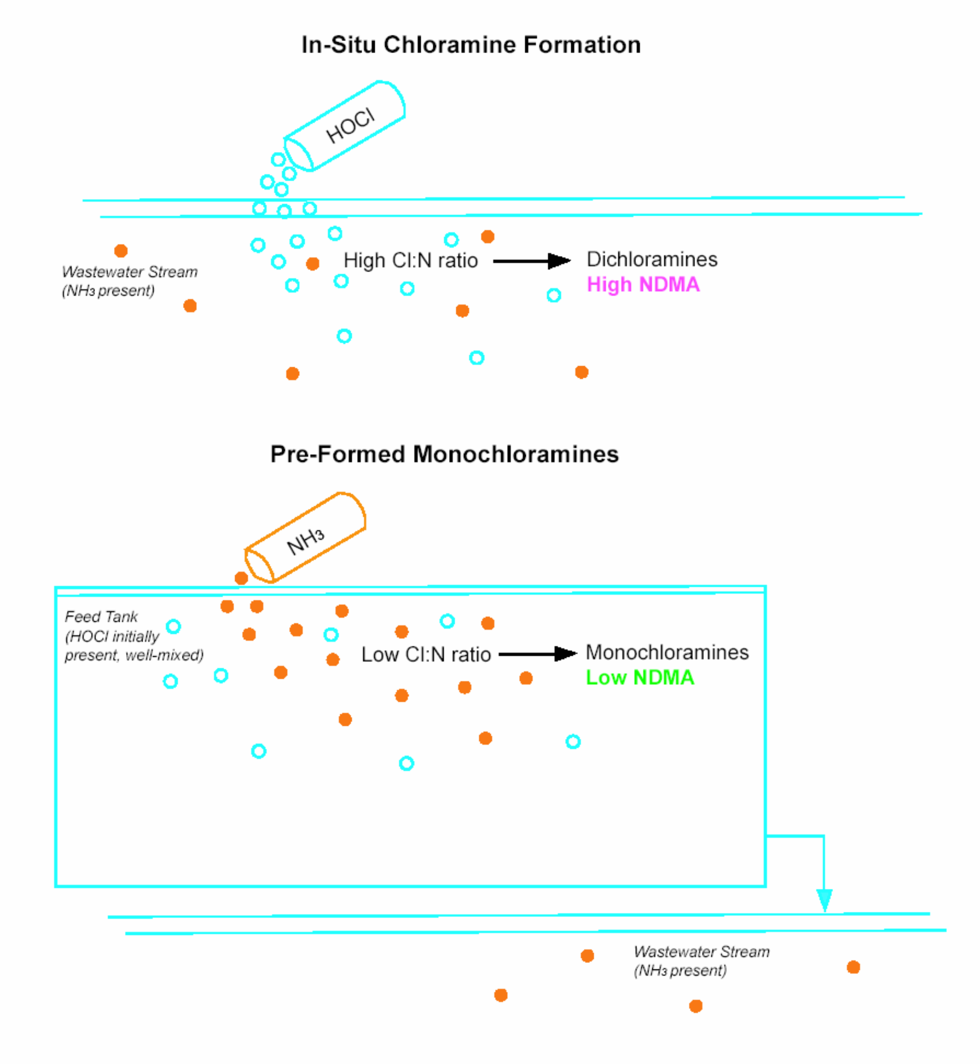


Figure 5-7. Reducing NDMA formation by preforming monochloramines.

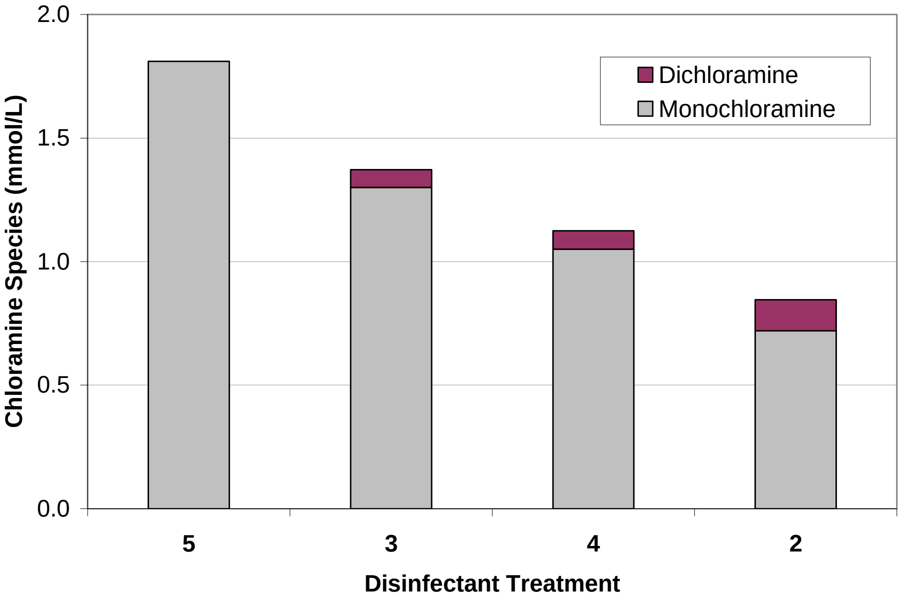


Figure 5-8. Monochloramine and dichloramine species measured in disinfectant treatment.

5.3.3 Studies Assessing NDMA and NDMA Precursor Removal Using MF, RO, and UV Treatment

The fate of NDMA and NDMA precursors during MF, RO, and UV treatment was investigated by sampling at OCWD, WBMWD, and the City of Scottsdale, AZ, treatment facilities. MF units are not designed to remove NDMA or NDMA precursors but serve as a pretreatment step to remove suspended solids and organic carbon prior to RO. While RO is not typically effective for low molecular weight organics like NDMA, RO membranes are often chosen by utilities because of their ability to remove a number of different organic chemicals from wastewater, including uncharacterized organics that may be NDMA precursors. UV treatment is currently the leading technology for removing NDMA. UV treatment systems are operating at OCWD and WBMWD.

5.3.3.1 NDMA Removal

Composite samples were collected before and after microfiltration at OCWD and Scottsdale. Several grab samples were also collected from West Basin. Prior to microfiltration, NDMA concentrations ranged from 20 to 100 ng/L at OCWD and West Basin. NDMA concentrations at Scottsdale were much higher, ranging from 140 ng/L to 360 ng/L.

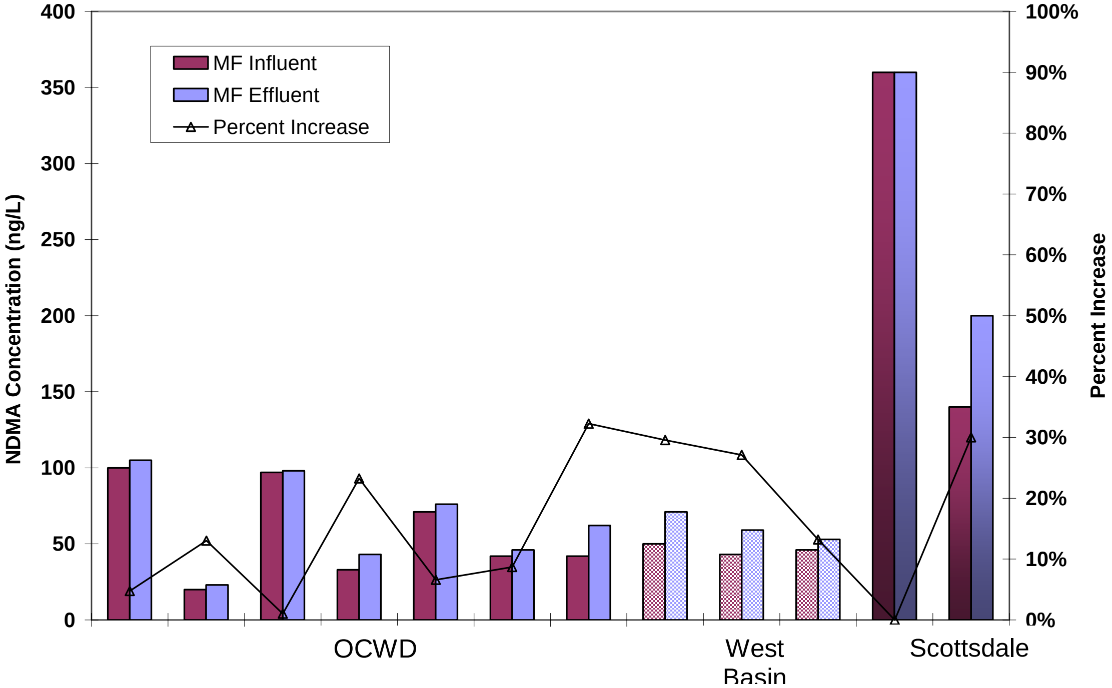


Figure 5-9. NDMA formation during microfiltration at OCWD, West Basin, and Scottsdale.

NDMA was not removed by microfiltration. On the contrary, NDMA concentrations increased up to 32% across microfiltration, with an average increase of 16%. The likely explanation is that NDMA forms across the microfilters because chlorine is added prior to microfiltration in order to keep microbial growth from fouling the membranes (West Basin Municipal Water District, 2002).

Average concentrations of NDMA entering RO systems at OCWD, Scottsdale, and West Basin ranged from 50 to 100 ng/L. Higher instantaneous levels were observed in grab samples collected from Scottsdale (greater than 350 ng/L of NDMA); however, these concentrations are not necessarily representative of average daily concentrations. Percent NDMA removal calculated at Scottsdale may not be representative due to the fact that the starting times of water sample collection were not staggered to capture the same flow of water. At OCWD and West Basin, approximately 50% of NDMA was removed by RO (Fig. 5-10).

As a result of RO treatment, effluent concentrations range from 13 ng/L to 50 ng/L. Based on the composite sample results, thin-film composite RO membranes remove some NDMA but do not achieve complete removal. UV systems are still needed to reduce NDMA concentrations below the California notification level of 10 ng/L.

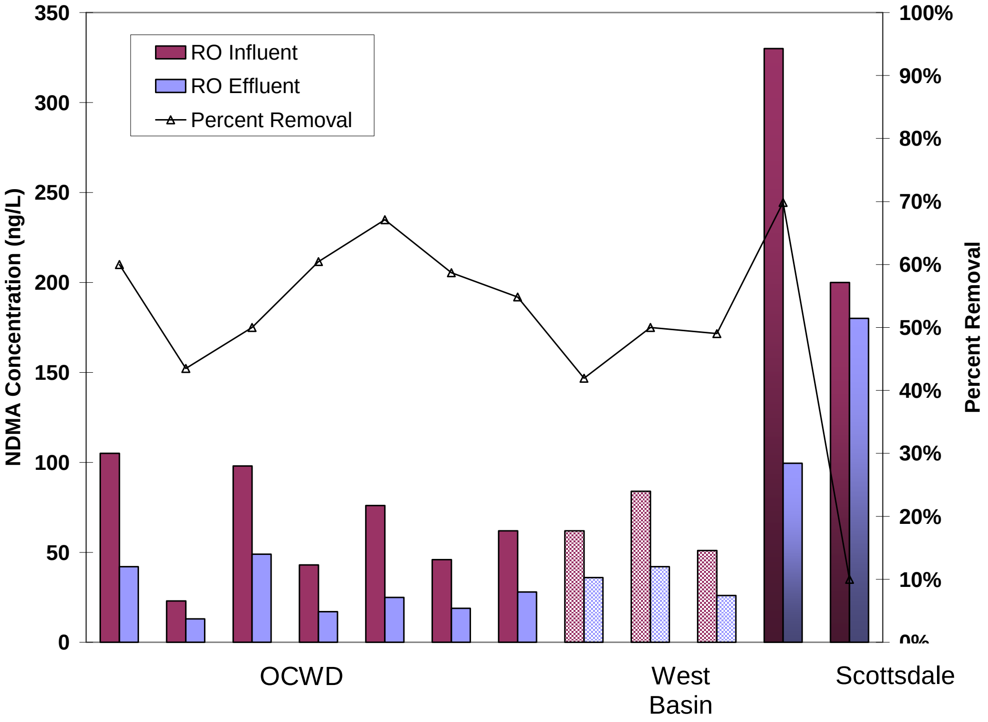


Figure 5-10. NDMA removal in RO systems (OCWD, West Basin, and Scottsdale).

UV systems are capable of meeting the California notification level. For example, at OCWD's low-pressure (LP) pilot-scale system, NDMA was reduced to a median concentration of 2.2 ng/L (maximum concentration of 28 ng/L), as shown in Figure 5-11. The power supplied by the UV reactor in this system was approximately 1.2 kWh/log of NDMA destruction/1000 gal.

However, pilot system effluent NDMA concentrations were not consistently below 10 ng/L; the effluent would still require blending prior to reinjection to meet the California notification level. Large-scale utilities such as OCWD may find it more cost-effective to blend before reinjection rather than overdesign the UV system to ensure complete NDMA removal at all times. NDMA removal rates at West Basin MWD using a Severn Trent pilot-scale UV system were similar, as shown in Figure 5-12. The electrical energy supplied by this UV system during sample collection days ranged from 0.17 to 0.38 kWh/log of NDMA removal/1000 gal.

The data from OCWD and West Basin illustrate that UV systems can be used to meet low NDMA discharge requirements fairly reliably. By altering UV system design, lamp configuration, and power output, utilities can save costs while continuing to meet their NDMA removal needs.

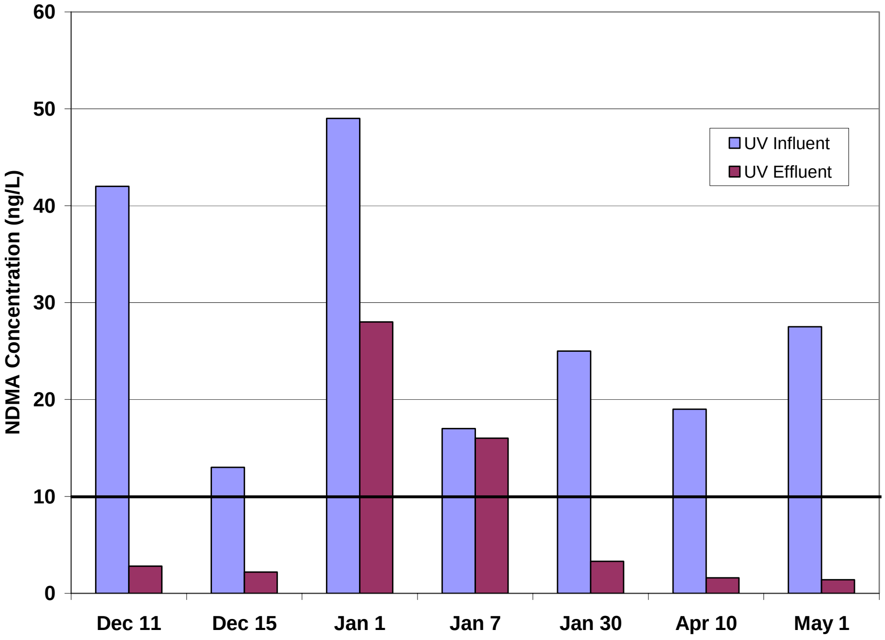


Figure 5-11. NDMA removal by UV at OCWD.

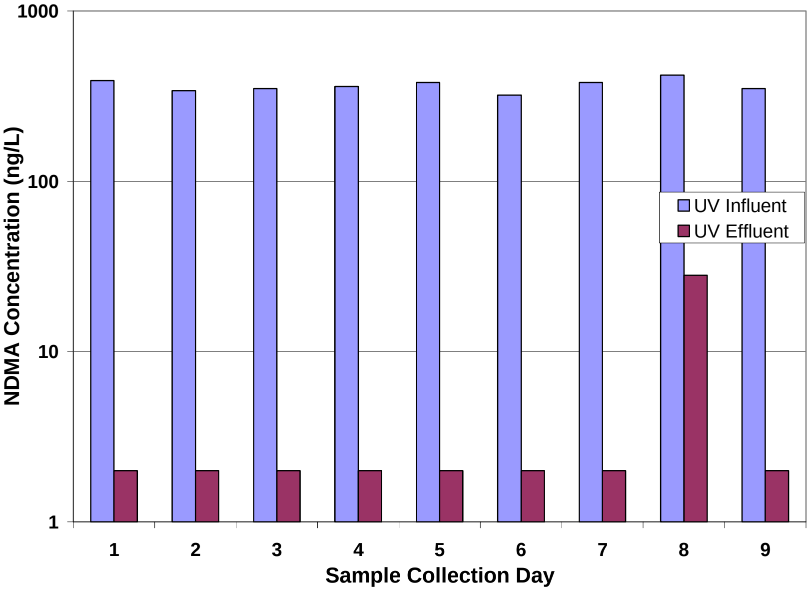


Figure 5-12. NDMA removal by UV at West Basin (Severn Trent UV system).

5.3.3.2 NDMA Precursor Removal

Unlike NDMA, some removal (an average of 51%) of NDMA precursors was seen during microfiltration. Removal was not consistent, however; removal at OCWD ranged from 12% to 95% (Fig. 5-13).

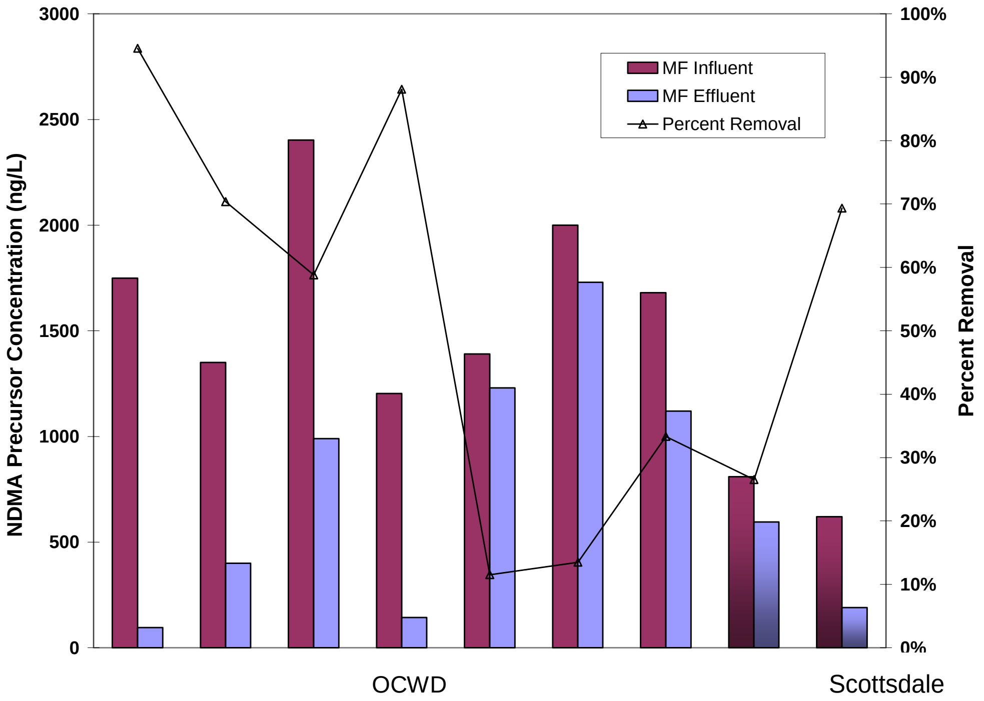


Figure 5-13. NDMA precursor removal during microfiltration at OCWD and Scottsdale.

Despite the decrease in total NDMA precursor concentrations due to MF at OCWD, the known NDMA precursor DMA was not removed during microfiltration. DMA concentrations were essentially unchanged by microfiltration, as shown in Figure 5-14, as would be expected, given the size of the DMA molecule. A median increase of 6%, which falls within the uncertainty of the analytical method, was measured in these samples collected from OCWD. This observation is consistent with findings reported in Chapter 4 that indicated that the NDMA precursors in secondary wastewater effluent include species other than DMA. The partial removal of these precursors during microfiltration suggests that the precursors were associated with particles or had an affinity for the MF membrane surfaces.

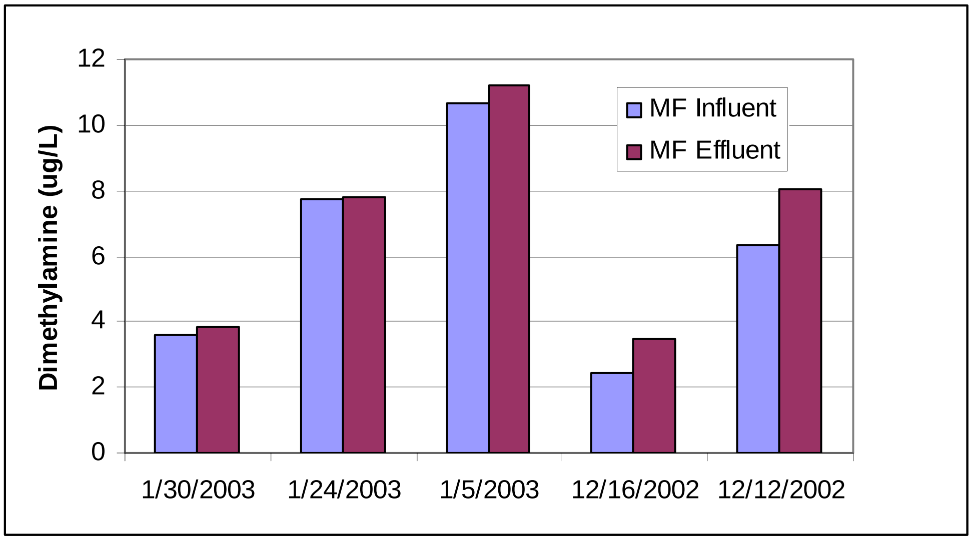


Figure 5-14. DMA removal during microfiltration at OCWD.

Since microfiltration membranes typically have a negative surface charge at pH 6 to 7, positively charged secondary and tertiary amines acting as NDMA precursors could have been partially removed by sorption to the membrane surface (Mitch et al., 2004). Precursors with a low molecular weight, such as dimethylamine, are not removed as easily as larger organic molecules.

NDMA precursor removal data were not available from the West Basin MWD. However, concentrations of NDMA precursors entering the West Basin facility were much higher than those measured at OCWD or Scottsdale, averaging 4560 ng/L with a standard deviation of 1450 ng/L. NDMA precursor concentrations at Scottsdale were relatively low (less than 1000 ng/L). However, concentrations of NDMA precursors at all three facilities were within the range of precursors detected in secondary effluent after conventional treatment, as discussed in Chapter 4.

Concentrations of NDMA precursors were also measured before and after RO treatment. Influent NDMA precursor concentrations ranged from 140 to 1730 ng/L, with an average daily concentration of 730 ng/L. NDMA precursor removal was always greater than 98%, with complete removal measured on some days, bringing final NDMA precursor concentrations to levels no higher than the NDMA levels actually present in the final effluent (Fig. 5-15).

As indicated by study results, NDMA precursors are effectively removed during RO treatment, with greater than 98% removal observed. The ability of RO membranes to remove NDMA precursors provides an added benefit that appreciable concentrations of NDMA (i.e., above the California notification level) will not form if chloramination is employed downstream of UV treatment. Since NDMA precursors were removed by RO treatment, NDMA precursor concentrations are not shown; NDMA precursor test results following UV were similar to NDMA concentrations.

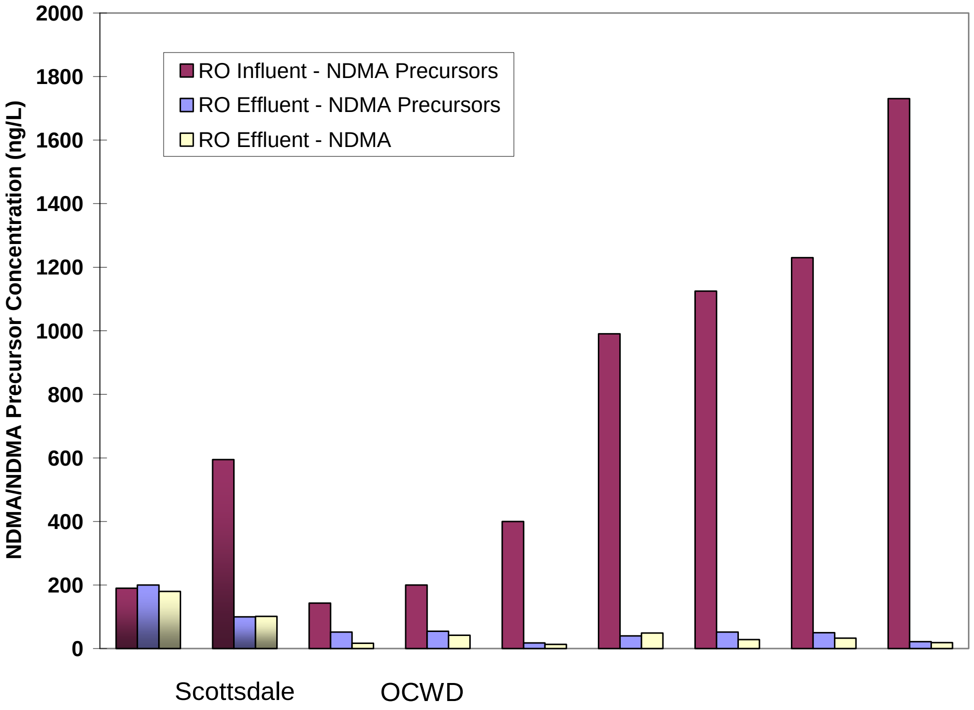


Figure 5-15. NDMA precursor removal during RO (Scottsdale and OCWD).

5.4 CONCLUSIONS

The treatment train MF-RO-UV is effective in removing NDMA and NDMA precursors during advanced wastewater treatment. MF was moderately effective in removing NDMA precursors; at OCWD, removal rates ranged from 12% to 95% with an average removal rate of 50%. RO is highly effective at removing the remaining NDMA precursors and moderately effective in removing NDMA. Greater than 98% removal of NDMA precursors was observed in the study; approximately 50% of NDMA was also removed. UV destruction of NDMA has been proven to be effective. UV destruction can be used to meet future California discharge limits for NDMA. UV destruction of NDMA precursors was not evaluated because RO removed NDMA precursors prior to UV treatment.

Utilities can further reduce NDMA concentrations using advanced treatment by slowing NDMA formation rates. Chlorine applied prior to MF has the potential to elevate NDMA concentrations by an additional 30% relative to unchlorinated MF influent. An average increase of 16% was observed in this study. NDMA formation can be slowed by reducing the amount of chlorine added to prevent microbial growth, practicing nitrification-denitrification prior to chlorine addition, preforming chloramines to prevent dichloramine from forming, or by maintaining an elevated or reduced pH. Control options such as these can reduce NDMA concentrations by up to 30 ng/L.

Future research needs for advanced treatment include investigations of the potential for utilities to meet discharge limits more cost-effectively using UV treatment or advanced oxidation (discussed in Chapter 6), the possibility of alternative disinfectants such as ClO_2 and shock chlorination, and the performance of other advanced treatment trains for removing NDMA.

CHAPTER 6

UV TREATMENT OF NDMA: A WATER QUALITY-BASED PHOTOLYSIS MODEL

6.1 INTRODUCTION TO UV TREATMENT OF NDMA

UV treatment is currently the leading technology for removing NDMA. For indirect potable reuse projects that are required to meet low (nanograms per liter) NDMA concentrations, UV treatment is the only viable and accepted treatment option. The physicochemical properties of NDMA (e.g., neutral, polar, small size) make many other treatment methods ineffective, including aeration, adsorption, and membrane treatment. Even RO membrane treatment using thin-film composite membranes can only remove approximately 50% NDMA at concentrations typically found in treated domestic wastewater (Chapter 5). Fortunately, the chemical structure of NDMA makes the compound highly susceptible to UV treatment via energy-efficient photolysis of the N-N bond (Fig. 6-1).

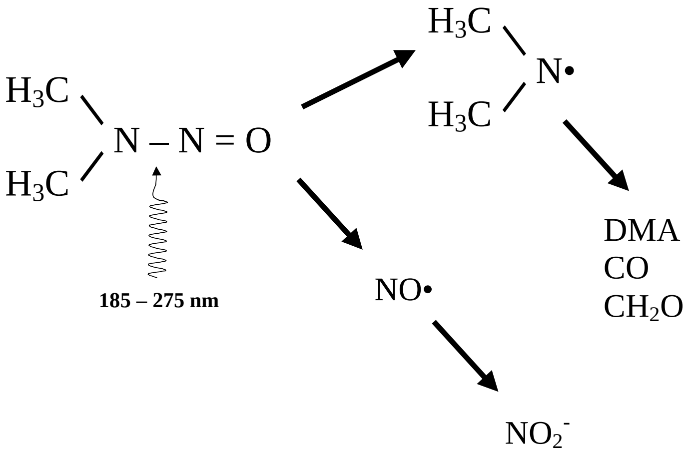


Figure 6-1. The pathway for direct NDMA photolysis (Chow, 1973; Hanst and Spence, 1977).

NDMA strongly absorbs UV light from 185 nm to 275 nm, with an absorption peak near the 228-nm wavelength (Fig. 6-2). NDMA also weakly absorbs light from 330 nm to 400 nm, centered at 332 nm (Calgon Carbon Corporation, 2000; Sharpless and Linden, 2003). UV light with wavelengths within this absorption band will attack NDMA directly, breaking the N-N bond and destroying the NDMA molecule.

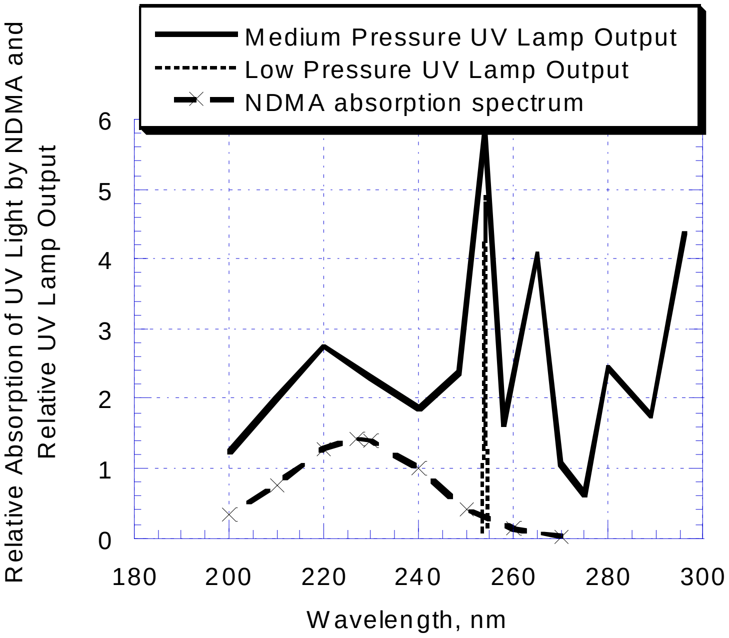


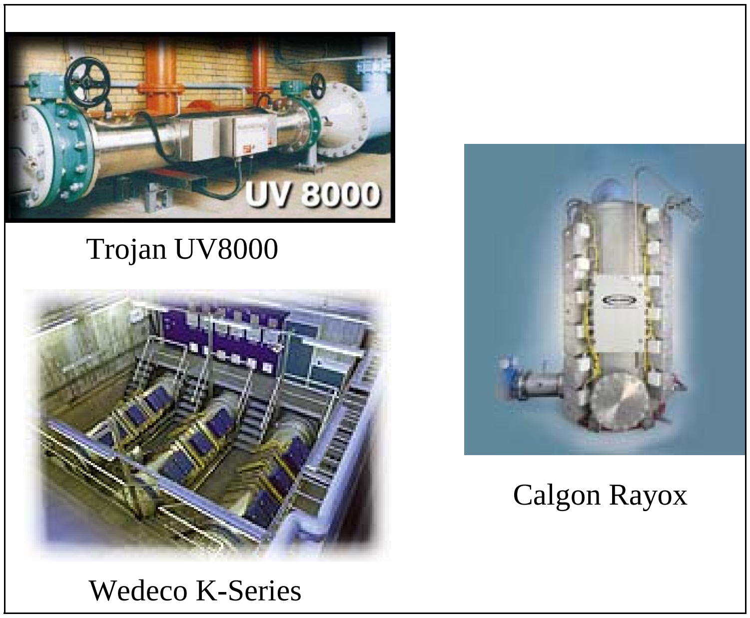
Figure 6-2. Absorption spectra of NDMA with low- and medium-pressure UV lamp output (Whitley Burchett & Associates, 2000).

6.1.1 Historical Developments in UV Applications for NDMA

Early work conducted by the OCWD demonstrated diurnal fluctuations in NDMA concentrations in open basins at Water Factory 21. Lower concentrations were observed during the day and higher concentrations were observed at night, indicating that the UV wavelengths present in sunlight were capable of some degree of NDMA destruction. OCWD measured complete removal of NDMA after less than 3 h under full sunlight conditions, starting with an initial NDMA concentration of 600 ng/L (Soroushian et al., 2001). Based on the results of this test, wastewater was channeled into open holding basins with a theoretical retention time of 1.5 h. This full-scale system resulted in moderate NDMA removal, ranging from 12% to 65% as measured using grab samples (Soroushian et al., 2001). The effectiveness of natural UV for NDMA degradation in surface waters is limited by the depth of penetration of UV light. For example, beam attenuation coefficients for UV-B wavelengths (280 to 320 nm) range from 0.26 to 17.2 m^{-1} in natural waters (Smith et al., 1999), resulting in 90% attenuation (absorption or scattering) in the first 1 to 40 cm, depending on water clarity and TSS concentration.

The history of NDMA treatment using UV irradiation involves a variety of UV technologies and highlights lessons learned as technologies which were developed for other purposes (disinfection or advanced oxidation of contaminants) were applied to NDMA. The biocidal effects of UV have been known since the late 1800s (WHO, 2002). Although it is commonly accepted as a disinfection method for wastewater, UV has not been widely used for drinking water treatment in the United States. Recently, with the need to achieve better inactivation of *Cryptosporidium* and remove emerging contaminants such as 1,4-dioxane, MTBE, and NDMA, UV treatment has been increasingly applied to groundwater remediation and drinking water treatment projects, usually in combination with hydrogen peroxide (H_2O_2).

Given this progression of UV treatment usage and the large number of UV equipment vendors, a wide variety of reactor configurations is currently available. Some examples are shown in Figure 6-3.



Trojan UV8000

Wedeco K-Series

Calgon Rayox

Figure 6-3. Examples of commercially available UV treatment systems.

A comparison of treatment efficacy of different UV reactors for removal of NDMA is difficult given the limited number of installations, proprietary nature of the technologies, disparity in reactor size and configuration, UV lamp type, and variations in water quality and concentrations of target contaminants.

Low-pressure UV produces light in a narrow band of wavelengths centered at 254 nm, a wavelength that is easily absorbed by NDMA (Fig. 6-2). With the discovery of the efficacy of low-pressure high-output (LPHO) UV lamps for NDMA removal, most recent applications of UV technology for NDMA treatment have used LPHO lamps. Low-pressure UV systems have been recently implemented at utilities for NDMA at La Puente, CA, WBMWD, OCWD, and Los Alamitos, CA.

Medium pressure (MP) UV lamps produce UV light at a variety of wavelengths in the range of 200 to 270 nm, overlapping with the absorption spectrum for NDMA (Fig. 6-2). Several utilities have tested the ability of UV to destroy NDMA using medium-pressure UV (Suburban, CA, La Puente, CA, and Six Nations, Ontario, Canada). Medium-pressure UV lamps have also been used at several groundwater remediation systems in California to treat NDMA and other contaminants, including the Aerojet site in Rancho Cordova and the San Gabriel Valley. In these systems, NDMA concentrations have declined from as high as 100–1000 ng/L to below the detection limit (0.5–10 ng/L). Initial applications of UV for NDMA removal using MP lamps were found to be effective but more costly than low-pressure lamps. The primary cost driver for UV treatment systems is electricity consumption. Other operational and maintenance (O&M) costs are typically a secondary concern. Because LPHO UV treatment systems use more lamps than MP systems to produce an equivalent power and comparable NDMA removal, other components of O&M (e.g., lamp cleaning, replacement) can factor into the cost equation more heavily.

6.1.2 Electrical Energy Requirements for NDMA Destruction (EE/O)

Electricity requirements for UV treatment systems are typically expressed as electrical energy per order of magnitude reduction in NDMA concentrations (EE/O), normalized by flow rate. The units of reported EE/O values are typically kWh/order/kgal. EE/O values are the industry's standard method for comparing treatment costs of different UV technologies and accounting for variations in water quality and reactor performance. By multiplying the EE/O by the price of electricity and the order of required NDMA removal, unit treatment costs can be determined (Bolton, 2002; Bolton and Stefan, 2002).

EE/O values are typically determined experimentally. For a flow-through reactor, the EE/O can be empirically expressed by the following equation (MWH, 2005):

$$EE/O = \frac{P}{Q \times \log \frac{C_i}{C_f}} \qquad (1)$$

where

P = Lamp power (kW)
Q = Flow rate (kgal per h)
C_i = NDMA concentration in UV influent (ng L^{-1})
C_f = NDMA concentration in UV effluent (ng L^{-1})

EE/O values can be determined experimentally by varying the UV dose and determining NDMA removal. A semilog plot of NDMA removal versus UV dose yields a straight line whose slope is the EE/O, as shown below with data developed by WBMWD (Fig. 6-4).

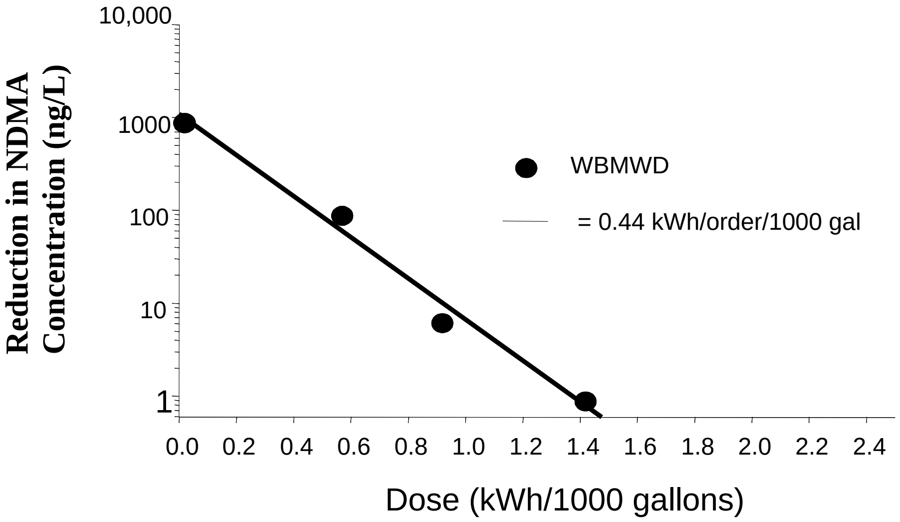


Figure 6-4. Empirical EE/O determination using data from WBMWD.

EE/O values are a result of several variables, including water quality, flow rate, reactor geometry, lamp type, and lamp power. The range of reported EE/O values for several pilot-scale and full-scale UV treatment systems illustrates the diversity of UV treatment system operating conditions, as shown in Table 6-1 (Calgon Carbon Corporation, 2002; Trojan Technologies, Inc., 2001).

Table 6-1. Representative EE/O Values for NDMA

Location	Lamp Type	EE/O (kWh/order/kgal)
OCWD, Vendor A	MP	1.28
OCWD, Vendor B	LPHO	0.5–0.8
OCWD, Vendor C	MP	1.1
WBMWD, Vendor A	MP	0.44
WBMWD, Vendor B	MP	0.61
WBMWD, Vendor C	LPHO	0.07
La Puente Valley MWD	MP	0.3
La Puente Valley MWD	LPHO	0.06–0.4

EE/O values have continued to decrease as UV treatment systems are tailored to remove NDMA and as treatment system optimization is performed. For example, vendors have improved baffling and inlet and outlet conditions to improve mixing and avoid short-circuiting. Utilities have improved the water quality supplied to the UV reactor, primarily via upgrades in advanced treatment processes made for other reasons, such as newer membrane technologies for MF- RO treatment.

6.1.3 UV Treatment Costs

Since UV systems have already been proven to destroy NDMA, utilities are now concerned with fine-tuning UV operations with the help of vendors or implementing additional pretreatment to make their systems more cost-effective. To determine the cost of using UV, a utility typically performs a series of experiments to determine empirically the EE/O needed for the site-specific water quality and treatment requirements. Since EE/O is a function of transmittance (the relative abundance of compounds that compete for UV light at the desired wavelength, such as nitrate), UV treatment costs for utilities can vary dramatically. For example, NDMA concentrations in a groundwater supply in Toronto, Canada, were reduced from over 10,000 ng/L to 14 ng/L (2.85 orders of removal) at a cost of \$0.35/1000 gal (\$115/acre-ft). In contrast, NDMA concentrations at a Toronto wastewater facility were reduced from 30,000 ng/L to 250 ng/L (2.08 orders of removal) at a cost of \$4.00/1000 gal (\$1300/acre-ft) (Smith, 1992).

During this project, two full-scale UV treatment systems for NDMA removal in indirect potable reuse projects have been bid, designed, and are under construction. A 70-MGD facility is being constructed by OCWD as part of the Phase I Groundwater Replenishment

Project (formerly referred to as Water Factory 21), and a 12.5-MGD facility is being constructed by WBMWD as part of their Phase IV expansion to ultimately provide 100% recycled water for the West Coast Basin seawater barrier project. The design basis used at WBMWD is similar to that used at OCWD, resulting in projects that differ only in capacity. The sizing and cost details for these two projects are summarized in Table 6-2.

Table 6-2. Capital and Annual O&M Costs for the OCWD and WBMWD UV Treatment Systems

Parameter	OCWD	WBMWD
Design EE/O	0.25 kWh/kgal/order	0.25 kWh/kgal/order
Log NDMA removal	1.2	1.3–1.7
Capital costs ($ 2005)	$18,200,000	$2,600,000
Annual O&M costs ($ 2005)[a]	$1,500,000	$165,000

[a] Annual O&M costs were estimated using a unit electricity cost of $0.10/kWh.

The annual cost for these systems normalized by treatment system flow rate is approximately $0.04 to $0.06/kgal ($12 to $19/acre-ft) for 1.2 to 1.7 log removal, which is relatively inexpensive compared to the overall treatment costs for advanced wastewater. Treatment costs are a function of both the physical reactor characteristics and water quality, with energy costs a function of lamp type, lamp power, and reactor size required to achieve the necessary reductions in NDMA concentrations. Some example net present value treatment costs (25 years at 7.25%) were calculated for a groundwater ion-exchange–UV treatment plant sized to remove 1 order of magnitude of NDMA at 9 MGD. Figures 6-5 and 6-6 show electricity costs as a function of EE/O (McGuire Environmental Consultants, 2001).

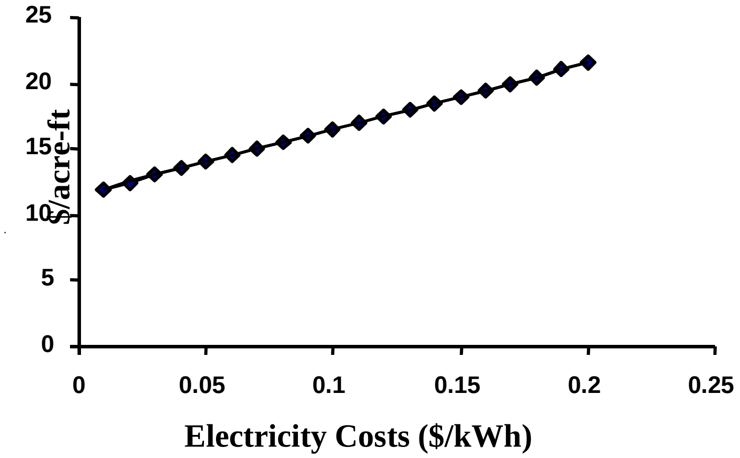


Figure 6-5. NDMA treatment costs as a function of the cost of electricity. The EE/O is held constant at 0.3 kWh/order/kgal.

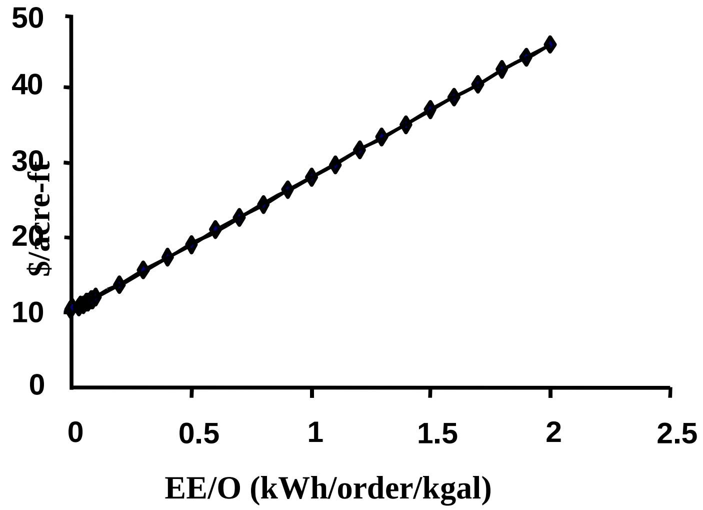


Figure 6-6. NDMA treatment costs as a function of EE/O. The cost of electricity is held constant at $0.09 kWh.

Over a typical range of electricity costs and EE/O values, treatment costs are predicted to be a stronger function of water quality than electricity costs. This underscores the importance of evaluating costs as a function of water quality during the conceptual design phase of any project for NDMA removal.

6.2 DEVELOPMENT OF A WATER QUALITY-BASED MODEL

This chapter presents the development, assessment, and application of a water quality-based UV treatment model for NDMA that can be used to predict NDMA removal rates and treatment costs as a function of water quality (Task 5). The spreadsheet model developed during this task is included as Appendix D. The objectives were to enable utilities and other water quality professionals to accomplish the following:

- Design a UV reactor (i.e., volume, number of lamps) and determine the power requirements needed to achieve a specified reduction in NDMA.
- Quantify the impact of changes in water quality on UV dose requirements and the associated UV treatment costs.
- Model the expected performance of a given reactor for removing NDMA.
- Evaluate tradeoffs of using UV vs. advanced oxidation (i.e., adding H_2O_2 to the UV system).

Utilities currently need to determine the answers to these questions experimentally or work closely with an experienced consultant and/or UV system vendor. If the utility is interested in answering these questions during the conceptual design phase or has not yet selected a vendor–UV system configuration, the utility would probably need to rely on professional judgment and might not be able to answer these questions quantitatively. The UV treatment model described in this section is meant to assist utilities by providing a basis for independent calculations to assess these issues quantitatively.

The UV model developed in this project is based on a theoretical expression for the destruction rate of NDMA as a function of water quality (concentrations of competitive absorbers), photochemistry (extinction coefficients, quantum yields), and UV reactor characteristics (number of lamps, lamp power, lamp radiant efficiency, and reactor configuration). The model is set up to calculate the approximate power requirements of the system, the effluent NDMA concentration, and hydraulic characteristics of the reactor. The user must specify values for the other two variables as well as influent water quality composition or transmittance, flow rate, and reactor volume.

6.2.1 Modeling a UV Reactor as Several Tanks in Series

NDMA removal in a UV reactor is a function of the reactor's hydraulic configuration. The most efficient UV reactor configuration is a plug flow reactor (PFR), in which a batch of water travels through the reactor without mixing with the water in front of it or behind it. In reality, some mixing does occur along the direction of travel, since not every water particle moves forward at a constant velocity. These flow irregularities reduce the overall reactor performance for most chemical reactions. The other extreme configuration for a UV reactor (i.e., the least efficient scenario for contaminant destruction) is a completely mixed flow reactor (CMFR). In a CMFR, water enters the reactor and is instantly and uniformly mixed with the rest of the reactor contents. Theoretical calculations for these two cases of reactor configuration simplify the general calculation of reactor performance as a function of percent mixing. These calculations demonstrate that a PFR provides an upper bound for reactor performance as a function of mixing and that a CMFR provides a lower bound for reactor performance (see, for example, MWH, 2005; Nazaroff and Alvarez-Cohen, 2000). The performance of most reactors is somewhere between these two extremes and can be modeled as several CMFRs in series, as shown in eq 2 (MWH, 2005).

$$\frac{C_{out}}{C_{in}} = \frac{1}{(1 + k\,\tau/n)^{n}} \tag{2}$$

where

C_{in} = Influent concentration (ng L^{-1})
C_{out}= Effluent concentration (ng L^{-1})
k = First-order rate constant (min^{-1})
τ = Average residence time of water within the reactor (min)
n = Equivalent number of CMFRs in series

The equivalent number of CMFRs in series, *n*, can be determined in practice by adding a pulse mass or continual concentration of a conservative tracer to the influent and measuring tracer concentrations in the effluent over time. The effluent concentration distribution is compared with theoretical tracer curves that were developed using different values for *n*. The value of *n* corresponding to the curve with the best fit is chosen to characterize empirically the hydraulic characteristics of the UV reactor. Since mixing within the reactor may be a function of flow rate, values of *n* may change with flow rate. Tracer tests should therefore be performed at flow rates similar to the expected operating conditions.

6.2.2 Impact of Water Quality on NDMA Destruction

Molecules in the water matrix may absorb UV light, competing with NDMA for the UV energy that is supplied to the reactor. The abilities of different compounds to absorb a particular wavelength of light is described by molecular extinction coefficients. The molar concentration, extinction coefficient, and light path length through the water sample determine the absorption of light (i.e., the logarithm of the ratio of incident light intensity to transmitted light intensity) by a specific compound or ion. Common absorbers, molecular masses, and their molar extinction coefficients are listed in Table 6-3 (Cushing et al., 2001; MWH, 2005).

Table 6-3. Extinction Coefficients for Some Potential Competing UV Absorbers in Recycled Water

Compound	Molecular Mass, g mol^{-1}	Extinction Coefficient at 254 nm, L mol^{-1} cm^{-1}
NDMA	74	1974
Nitrate	62	3.8
Fe(II)	56	448
Fe(III)	56	2950
PCE	166	205
TCE	131	9
DOC as C	12	240
H_2O_2	34	16.6
OCl^-	51	155
HOCl	52	53
Water	18	6.1×10^{-6}

The relative UV absorbance of each compound is dependent on the molar concentration in the water and the extinction coefficient at the wavelength of interest. Both must be considered to determine the key competitive absorbers. For example, even though the extinction coefficient of water is 8 orders of magnitude lower than that of NDMA, concentrations are typically 10 orders of magnitude higher (e.g., 55 mol of water/L compared with 1.3 nmol of NDMA/L), making water a potential competitor of NDMA for UV light. The fraction of light absorbed by NDMA in the presence of other molecules can be described by eq3.

$$f_{NDMA} = \frac{\varepsilon(\lambda)_{NDMA} \times C_{NDMA}}{\sum_i \varepsilon(\lambda)_i \times C_i} \qquad (3)$$

where

ε = Molar extinction coefficient (L mol^{-1} cm^{-1}) at wavelength λ

C_i = Molar concentration (mol L^{-1}) of compound *i*

f_{NDMA} = Fraction of light absorbed by NDMA

Σ_i = Sum for every compound *i* that absorbs UV light

Concentrations of other UV absorbers listed in Table 6-3 are highly dependent on the type of water to be treated (e.g., secondary effluent, tertiary treated wastewater, RO-treated wastewater). In RO-treated wastewater intended for indirect potable reuse applications, concentrations of common ions such as nitrate, nitrite, iron, and total organic carbon (TOC) are either nondetect or close to detection limits and are therefore not significant absorbers at 254 nm. Since RO membranes are subject to membrane oxidation and damage when exposed to free chlorine or chloramines, hypochlorite is not expected to be a significant absorber of UV light in RO permeate. When fewer competitive absorbers are present, such as in RO effluent, it is easier to predict NDMA removal rates using a theoretical photolysis model.

Utilities with multiple competitive absorbers present may wish to measure transmittance of a water sample and use this as a model input instead of entering the concentrations of each compound listed in Table 6-3. UV light at the 254-nm wavelength is shown through a water sample (typically 1-cm light path length); the incident light intensity and transmitted light intensity are measured with a spectrophotometer. Transmittance is calculated using eq 4 (MWH, 2005).

$$\%UVT = \frac{I(\ell)}{I_0} x100\% \tag{4}$$

where

$\%UVT$ = Percent UV transmittance at 254 nm

$I(\ell)$ = Transmitted light intensity (mW cm^{-2}), measured after passing light through a known depth of water ℓ (typically 1.0 cm during laboratory testing)

I_o = Incident light intensity (mW cm^{-2})

Since the total absorbance of light is the negative logarithm of transmittance, the fraction of light absorbed by NDMA in the water sample can be calculated as follows:

$$f_{NDMA} = \frac{\varepsilon(\lambda)_{NDMA} \times C_{NDMA} \times \ell}{-\log(\%UVT)} \tag{5}$$

where all terms have been previously defined.

6.2.3 Determining the Rate Constant for NDMA Destruction

At NDMA concentrations below 1 mg/L, the kinetics of NDMA photolysis are first order (Bolton, 2001). The power supplied to the reactor to photolyze NDMA in the presence of other absorbers determines the first-order rate constant for NDMA destruction. The calculation takes into account several losses of UV light within the reactor. Typically, UV reactors are designed to reflect light off of interior surfaces so that the light is essentially trapped inside the reactor until it is absorbed by the water matrix. In reality, some light is absorbed by the reactor surfaces, lamp sleeves, or precipitate that forms on the lamp sleeves (MWH, 2005). These losses are characterized in the model by the electrical efficiency.

In addition, only a fraction of the light radiated from the UV system is of the correct wavelength to destroy NDMA. For low-pressure monochromatic UV lamps, most of the UV light is at the appropriate wavelength to act on NDMA (254 nm). Approximately 30% of the energy radiated by medium-pressure lamps is the correct wavelength to destroy NDMA. This is characterized in the model by the value of radiant efficiency. Finally, light that reaches an NDMA molecule may or may not result in photolysis. The probability that molecular photolysis may occur upon contact is described by the quantum yield.

Using water quality data and estimates of reactor efficiency and quantum yield, the power supplied to the UV reactor can be related to the NDMA destruction rate using eq 6 (MWH, 2005).

$$k = \frac{\phi(\lambda)_{NDMA} \eta R_{eff} P f_{NDMA}}{C_{NDMA} N_{av} V h \nu} \tag{6}$$

where

k = First-order rate constant for NDMA destruction (s^{-1})
$\phi(\lambda)_{NDMA}$ = Quantum yield for NDMA (mol einstein^{-1}) at wavelength λ
η = Electrical efficiency (unitless)
R_{eff} = Radiant efficiency (unitless)
P = Power supplied to UV reactor (W)
f_{NDMA} = Fraction of light absorbed by NDMA (unitless); calculated using eq 3 or eq 5
C_{NDMA} = Molar concentration (mol L^{-1}) of NDMA
N_{av} = Avogadro's number, 6.02×10^{23} (photons einstein^{-1})
V = Reactor volume (L)
$h\nu$ = Planck's constant, $6.62 \times 10^{-34} \times$ UV light frequency (J)

If the power output of a particular low-pressure UV system is known, the rate constant for NDMA destruction can be calculated using eq 6. Conversely, given the NDMA degradation rate constant, the equation can be used to estimate UV system power requirements. Power consumption can then be translated into an EE/O value to characterize system performance and electrical operating costs.

6.2.4 Potential Uses of the Photolysis Model

Utilities may want to use the photolysis model for different purposes, including predicting electricity requirements and the associated costs or predicting the performance of a given reactor. Two versions of the model are therefore included in Appendix D. In the first version (Table D-1), the user enters the NDMA influent concentration, influent water quality, known NDMA effluent goal, fixed flow rate, and some assumptions about reactor configuration (i.e., CMFR or PFR) and electrical efficiency. The model predicts the necessary reactor volume, residence time, power requirements, and electricity costs.

The second version of the model (Table D-2) can be used to predict the performance of a given reactor of known size, configuration, power input, influent water quality (including NDMA concentration), flow rate, and electrical efficiency. The model calculates the effluent NDMA concentration and electricity costs per log removal. This scenario can be used to validate model predictions using empirical data from a given UV treatment system. This scenario may also be used as a baseline for evaluating vendor claims.

A third use of the model could be to determine the value of *n* (the equivalent number of tanks in series) which corresponds to the reactor's hydraulic configuration and flow rate. Using empirical data for the reactor size, power input, influent water quality, effluent NDMA concentration, flow rate, and electrical efficiency, *n* can be calculated (Table D-3). As demonstrated in the following sections, modeling is not a valid substitute for conducting a tracer test of the UV reactor. However, determining the best-fit value of *n* to empirical data can be used to conceptually illustrate how reactor hydraulics can change as a function of flow rate.

6.3 MODEL RESULTS

6.3.1 Determining the Impact of Water Quality on EE/O and Cost

The model allows the user to calculate the impact of water quality on EE/O and the associated electricity costs. The user can input concentrations of various competitive UV-absorbing molecules or analytical results for percent UV transmittance. Total absorption can then be calculated and used to determine the fraction of light absorbed by NDMA. As an example, the model was run to determine power requirements as a function of percent UV transmittance for a 500-gpm treatment system with an influent NDMA concentration of 100 ng/L and effluent requirement of 10 ng/L. In the example, hydraulic performance was assumed to have been characterized as *n* = 4; electrical efficiency and radiant efficiency were assumed to be 95% and 30%, respectively. Results are shown in Figure 6-7.

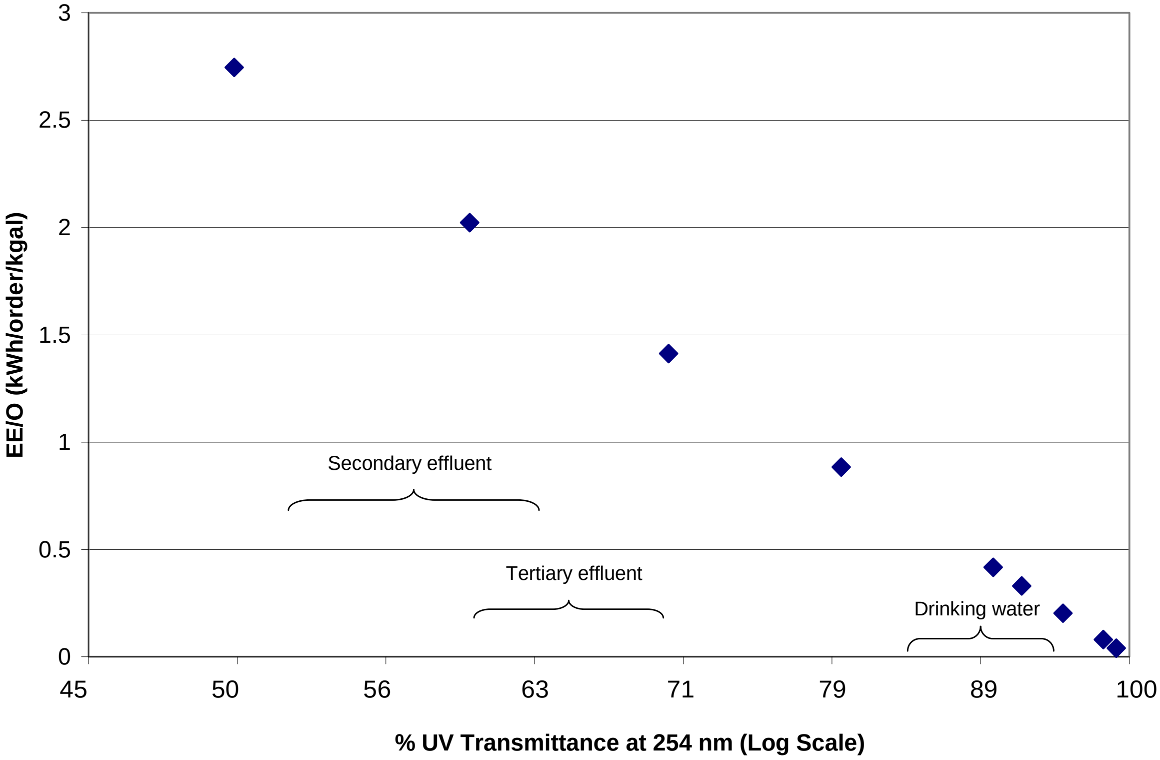


Figure 6-7. Dependence of EE/O on water quality.

For comparison, typical ranges of percent UV transmittance in secondary, tertiary, and advanced treatment effluent are also shown in Figure 6-7 (Sakamoto, 2000). Percent transmittance in highly treated wastewater effluents can be similar to or higher than that of drinking water. UV transmittance at OCWD ranged from 89 to 97% during UV testing; at WBMWD, percent UV transmittance of RO permeate was measured at ~98% (Loveland, 2002). The graph illustrates that electricity costs will increase exponentially with decreases in water quality (i.e., percent UV transmittance). Using the EE/O values shown in Figure 6-7 and assuming an average electricity cost of $0.09/kWh, UV treatment for 1 order of magnitude NDMA removal for a 1000-gpm system would cost approximately $70,000 per year (EE/O = 1.4 kWh/kgal/order) to treat tertiary effluent (70% UV transmittance) but would only cost approximately $4000 per year (EE/O = 0.08 kWh/kgal/order) to treat RO permeate (98% UV transmittance).

6.3.2 Calibrating the Model Using Empirical Data

The model can also be used to predict NDMA removal rates achieved by a particular UV treatment system with known reactor hydraulics, size, and lamp power. This approach can be used to estimate the accuracy of the model for a particular UV treatment system of interest or to verify vendor estimates of reactor performance.

Performance data from a demonstration-scale UV treatment system tested at OCWD were provided to the project team to compare with photolysis model predictions. Using reactor specifics and influent water quality data, model predictions were compared with the actual system performance data. OCWD commissioned the demonstration testing prior to selecting a commercial UV system for the full-scale facility. Wastewater entering the pilot system had already been passed through secondary treatment and tertiary treatment (filtration), followed by microfiltration and RO. The UV treatment system was designed to achieve a 1.3 log reduction of NDMA while keeping EE/O below 0.3. Since draft California recharge criteria may mandate advanced oxidation (UV and H_2O_2) for indirect potable reuse projects with a reclaimed water component greater than 50%, testing was done in the presence of 5 mg/L H_2O_2. Approximately 125 ng/L NDMA was added to the influent of the UV treatment system to ensure that NDMA concentrations were high enough to reflect UV system capabilities. Paired influent and effluent samples were collected from the UV treatment unit at varying flow rates (100 to 1000 gpm) while constant electrical energy was applied. Testing was repeated on three different days.

Influent water quality was fairly consistent during the vendor qualification testing. The percent UV transmittance at 254 nm was measured before each test. Results ranged from 93.4% to 97.3%. Influent NDMA concentrations ranged from 137 to 154 ng/L. A summary of the demonstration-scale unit characteristics that were used in the model are shown in Table 6-4. For confidentiality purposes, the vendor name and UV treatment system model number are not included.

Table 6-4. OCWD Demonstration Test Characteristics

Parameter	Units	UV Treatment System Characteristics
Influent Flow Rate	gpm	100–1000
Influent NDMA	ng/L	400–640
Other Water Quality Info.		% UV transmittance 93.4–97.3%, H_2O_2 = 5 mg/L
Lamp Type		LPHO
Power Supplied	kW	2.059
Reactor Configuration (*n*)[a]		1–999 (unknown)
Reactor Diameter (outer)	m	0.3
Reactor Length	m	1.52
Reactor Volume	L	34.2
Residence Time	s	1.7–17
Radiant Efficiency[b]		0.25
Electrical Efficiency		0.95
Predicted Rate Constant	s^{-1}	0.2–0.5
Predicted NDMA Effluent	ng/L	0.04–116
Measured NDMA Effluent	ng/L	2–87
Predicted EE/O	kWh/kgal/order	0.097–0.28
Measured EE/O	kWh/kgal/order	0.10–0.29

[a] This range of values for *n* covers the range of reactor configurations from CMFR (*n* = 1) to PFR (large *n*).

[b] The radiant efficiency was estimated to best fit the observed NDMA effluent concentrations between PFR and CMFR performance curves.

Model-predicted NDMA concentrations ranged from 0.04 to 116 ng/L, while measured NDMA concentration in the UV treatment system effluent ranged from 2 to 87 ng/L. The UV treatment system met study requirements: EE/O values ranged from 0.10 to 0.29 kWh/order/kgal, as shown in Table 6-4. Model-predicted EE/O values were similar, ranging from 0.097 to 0.28 kWh/order/kgal.

NDMA effluent concentrations were strongly influenced by the flow rate through the reactor (residence time). Influent NDMA concentrations were fairly constant during testing (from 137 to 154 ng/L). At lower flow rates (100 gpm; average residence time, 17 s), the reactor achieved greater than 90% removal. At higher flow rates (1000 gpm; average residence time, 1.7 s) approximately 45% removal of NDMA was achieved. This dependence was predicted by the model and observed during the pilot tests (Fig. 6-8).

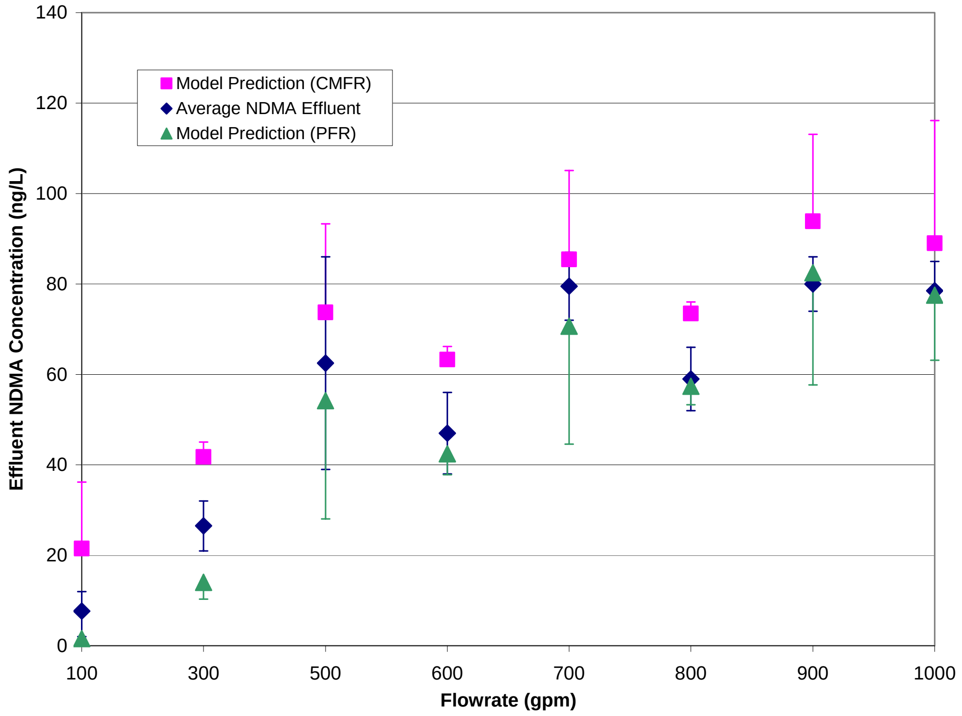


Figure 6-8. Comparison of modeled NDMA effluent predictions for different values of *n* with average measured effluent concentrations. Note: Influent NDMA concentrations ranged from 137 to 154 ng/L. Error bars correspond to maximum and minimum values.

Since the actual hydraulic configuration of the UV treatment unit had not been characterized, model predictions were made for CMFR and PFR configurations. The PFR configuration predicted a higher percent NDMA removal than the CMFR configuration, as discussed previously. The average measured NDMA removal was between these two extremes (i.e., PFR overestimated NDMA removal and CMFR underestimated NDMA removal).

Model-predicted percent NDMA removal was compared with measured percent NMDA removal for each individual test run. The results of several test runs could not be predicted by the model, particularly when NDMA removal was below 50%. The UV treatment system exceeded the model's prediction for PFR performance at these higher flow rates. Conversely, for one test run, the UV treatment system did not perform as well as the photolysis model predicted for a CMFR (Fig. 6-9).

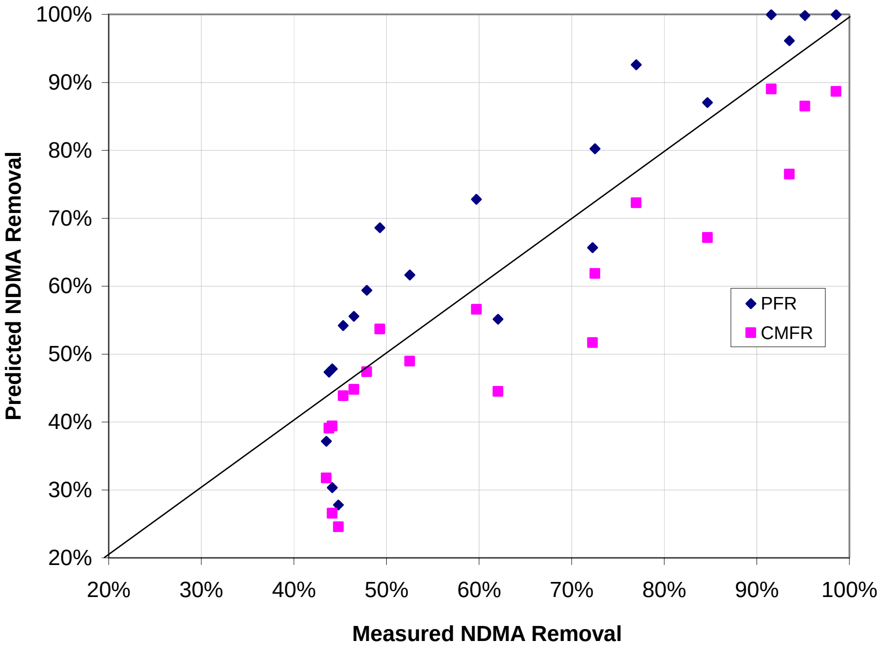


Figure 6-9. Comparison of model predictions and measured values of percent NDMA removal for different reactor configurations.

This indicates that although the model can be used to predict the approximate range of performance, the actual performance may vary within a wider range. One potential explanation is that influent water quality changed during the course of testing while the model assumes that water quality was constant. Percent UV transmittance was measured at the start of each test. If percent UV transmittance changed from 93.4% at the start of the test to 96.6% during the middle of the test as higher flow rates were tested, the model would predict the measured NDMA effluent concentrations. Alternatively, variations in electrical efficiency over time may occur due to precipitation onto the lamp sleeves. Model-predicted NDMA effluent concentrations spanned the range of measured NDMA concentrations when average NDMA concentrations were modeled for each flow rate tested. Overall, model predictions agreed well with measured values (as shown above in Table 6-4).

6.3.3 Assessing Reactor Hydraulics as a Function of Flow Rate

If the reactor hydraulics have not yet been characterized (e.g., a tracer test has not been performed at various flow rates), the most conservative approach is to model a PFR (large *n*) and a CMFR (*n* =1) to characterize the upper and lower bounds of actual hydraulic performance. However, model predictions can vary widely with different values of *n*. For example, as shown in Figure 6-9, model predictions for PFR performance and CMFR performance varied from 90% and 70% removal, respectively (measured NDMA removal of ~76% at 300 gpm with a residence time of 5.8 s). This range of predicted NDMA removal may be too broad to be an adequate design basis. If a utility planned to construct a UV system to treat a similar quality and quantity of water with a similar residence time, the UV reactor hydraulics would need to be better characterized. A third version of the model was developed to enable the user to calculate the best-fit value of *n* for a reactor based on empirical data. A copy of the model is provided in Appendix D (Table D-3).

Using the tanks-in-series model, values of *n* can be empirically determined using experimental data from the UV reactor of interest. For example, best-fit values of *n* were determined for each of the OCWD demonstration-scale tests using the model. Results were plotted to see if there was any noticeable correlation between flow rate or Reynold's number and the best-fit value for *n* (Fig. 6-10).

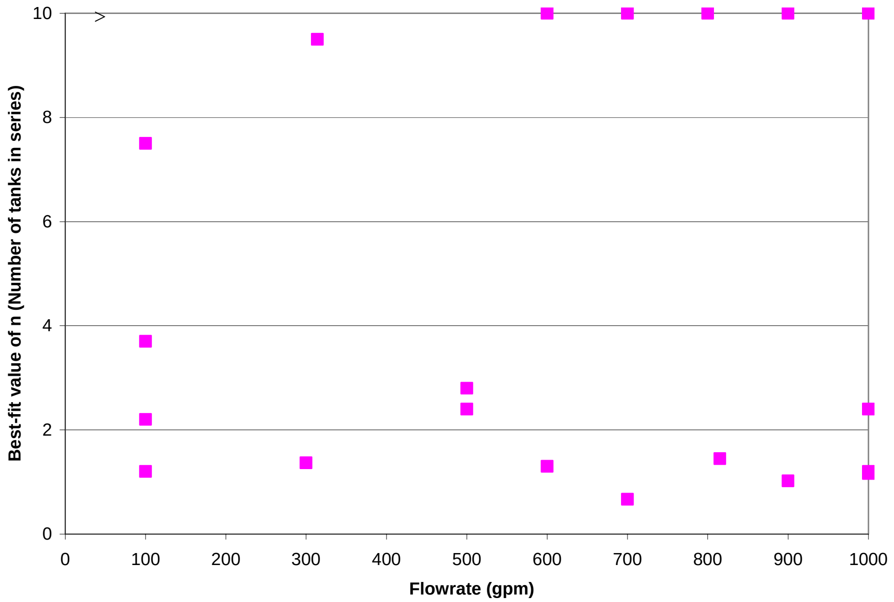


Figure 6-10. Model-determined best-fit values of *n* (number of equivalent CMFR tanks in series) as a function of flow rate.

As flow rate through the reactor increases, turbulence and the extent of lateral mixing may also increase, resulting in lower values of *n* (CMFR performance). On the other hand, the increased flow rate could eliminate low-flow stagnant zones and increase the plug flow nature of the reactor, resulting in higher values of *n*. However, as shown in Figure 6-10, no relationship was readily apparent. A more sophisticated model of reactor mixing is required to characterize the changes in flow pattern in this reactor. Alternatively, tracer tests could be performed at various flow rates to empirically determine the value of *n*.

6.4 MODELING ADVANCED OXIDATION PROCESSES

Draft California groundwater recharge and reuse criteria currently require utilities that are conducting recharge operations with greater than 50% reclaimed water component to employ post-RO treatment with advanced oxidation (UV and H_2O_2) to achieve established log reductions in targeted chemicals (CalDHS, 2003). However, CalDHS noted in the draft criteria that they are continuing to seek ideas on how to regulate advanced oxidation requirements to effectively address emerging contaminants (CalDHS, 2003). The benefits and drawbacks of adding H_2O_2 to supplement UV treatment are examined in the following section.

6.4.1 Impact of Hydrogen Peroxide on NDMA

Utilities facing draft California recharge regulations or water quality challenges from a variety of contaminants may need to implement UV treatment in combination with H_2O_2. Conceptually, the addition of H_2O_2 could reduce the effectiveness of the UV treatment system for NDMA, because H_2O_2 absorbs UV light, reducing the fraction of light available for NDMA photolysis. This effect would increase as the H_2O_2 concentration increased. On the other hand, NDMA destruction could be enhanced in the presence of H_2O_2 because NDMA can be oxidized by hydroxyl radicals that are generated by H_2O_2 in the presence of UV. The magnitude of this effect is dependent on the steady-state concentration of hydroxyl radicals.

Previous research has investigated the impact of H_2O_2 on NDMA removal rates (Sharpless et al., 2001; Sharpless and Linden, 2003). Experiments were carried out in a batch reactor for different lamps using drinking water spiked with NDMA. Researchers found that adding H_2O_2 slightly enhanced NDMA removal rates at low concentrations due to the reaction of hydroxyl radicals with NDMA. This was followed by a decline in performance at higher H_2O_2 concentrations as competitive absorption for UV light became the dominant effect (Fig. 6-11) (Sharpless and Linden, 2003).

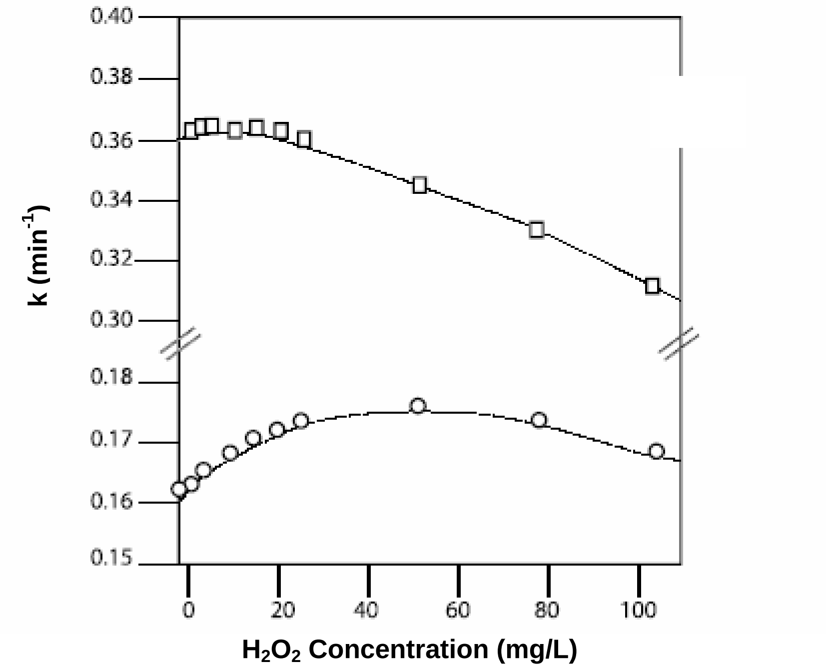


Figure 6-11. Simulated rate constant for NDMA destruction as a function of H_2O_2 concentration; LP (O), MP (□) (adapted from Sharpless and Linden, 2003).

Hydrogen peroxide preferentially absorbs shorter wavelengths of UV light. The absorption spectrum overlaps with the medium-pressure lamp output more than with the low-pressure lamp output (Sharpless and Linden, 2003). Competitive absorption therefore became the dominant effect at lower H_2O_2 concentrations in the medium-pressure system. As seen in

Figure 6-11, concentrations up to 50 mg/L of H_2O_2 resulted in a slight enhancement of system performance. For medium-pressure UV systems, an extremely small enhancement of UV system performance was observed at concentrations up to 10 mg/L of H_2O_2.

The reaction rate constant of hydroxyl radicals with NDMA is approximately 3.3×10^8 mol L^{-1} s^{-1} (Sharpless and Linden, 2003). Typical steady-state concentrations of hydroxyl radicals range from 10^{-12} to 10^{-11} mol L^{-1} (MWH, 2005). Multiplying these values yields a first-order rate constant for NDMA destruction by hydroxyl radicals that ranges from 10^{-4} to 10^{-3} s^{-1}, a negligible increase to the NDMA destruction rate constant from direct UV photolysis (0.2 to 0.5 s^{-1} in OCWD pilot studies described previously).

The same conclusion can be made for both low-pressure and medium-pressure systems, that is, NDMA removal is not greatly improved by the addition of H_2O_2. At high doses of H_2O_2 (e.g., 50 to 100 mg/L), treatment system performance may decline due to competitive absorption of UV light. However, concentrations typically used in advanced oxidation processes for highly treated wastewater are on the order of 1 to 5 mg/L.

6.4.2 Impact of Hydrogen Peroxide on NDMA Precursors

Advanced oxidation may offer advantages over traditional UV for destroying NDMA precursors. CalDHS originally proposed adding H_2O_2 because of its promise for degrading NDMA precursors, thus preventing the reformation of NDMA upon chloramine addition. However, as described in Chapter 5, the use of microfiltration and RO following conventional treatment has been shown to be effective in completely removing NDMA precursors, making it hard to quantify any benefits associated with using H_2O_2 as a redundant barrier against NDMA precursors.

If RO is not used in the treatment train prior to UV, utilities may be interested in evaluating the potential benefits of H_2O_2 for removing NDMA precursors. The approach described in the following section can be followed to evaluate the potential benefits of adding H_2O_2 to oxidize NDMA precursors or other unknown organic compounds.

6.4.3 Impact of Hydrogen Peroxide on Unknown Organic Compounds

The addition of H_2O_2 may provide water quality benefits by removing other organic compounds from treated wastewater, particularly compounds with low molecular mass (e.g., 300 daltons) that survive RO and UV treatment. Examples include 1,4-dioxane and selected pharmaceutically active endocrine-disrupting compounds. While these compounds are not readily susceptible to direct UV photolysis, the addition of H_2O_2 in the presence of UV generates hydroxyl radicals ($OH^{\cdot}$) that can oxidize the organic compounds.

A modeling exercise was conducted to estimate the predicted percent removal within the UV reactor as a function of H_2O_2 dose. Since the hydraulic residence time of the reactor is known, the percent removal can be determined using the tanks-in-series model (eq 2) for different values of n once the first-order reaction rate k has been determined. The first-order rate constant can be expressed as the product of the second-order rate constant k' and the steady-state hydroxyl radical concentration (Stefan et al., 1996).

The second-order rate constant was calculated assuming that the reaction between the unknown organic compound and a hydroxyl radical was bimolecular and diffusion controlled. These are valid assumptions for small, uncharged molecules in dilute solutions, such as RO permeate. The bimolecular reaction rate was determined using the following equation (Stumm and Morgan, 1981).

$$k' = \frac{4\pi N_{av}}{1000}\left(D_A + D_B\right)r_{AB} \tag{7}$$

where

k' = Bimolecular reaction rate constant (L^2 mol^{-2} s^{-1})
N_{av} = Avogadro's number (molecules mol^{-1})
D_A = Molecular diffusion coefficient (cm^2 s^{-1}) of compound A
D_B = Molecular diffusion coefficient (cm^2 s^{-1}) of compound B
r_{AB} = Radius of collision separation distance, assumed to be 5×10^{-8} cm based on molecular radii (Stumm and Morgan, 1981)

The molecular diffusion coefficients were estimated using an approximate molar mass-based correlation (Schwarzenbach et al., 1993), shown in eq 8:

$$\frac{D_{w,unknown}}{D_{w,known}} \cong \left(\frac{m_{known}}{m_{unknown}}\right)^{0.5} \tag{8}$$

where

$D_{w,\,unknown}$ = Molecular diffusion coefficient of unknown compound in water
$D_{w,\,known}$ = Molecular diffusion coefficient of known compound in water
m_{known} = Molecular weight of known compound
$m_{unknown}$ = Molecular weight of unknown compound

Using any known compound (e.g., trichloroethylene with a molecular mass of 131 g/mol and diffusion coefficient of 1×10^{-5} cm^2 s^{-1}), diffusion coefficients of 2.8×10^{-5} and 6.6×10^{-6} cm^2 s^{-1} were obtained for hydroxyl radicals (molecular mass of 17 g/mol) and the unknown organic compound (molecular mass of ~300 g/mol), respectively. Using these diffusion coefficients, a second-order, bimolecular reaction rate of $k' = 1.3 \times 10^{10}$ L mol^{-1} s^{-1} was obtained for a generic unknown organic molecule.

The steady-state hydroxyl radical concentration was estimated using eq 9 (Stefan et al., 1996). Due to the rapid formation and reaction of hydroxyl radical, it is appropriate to use a steady-state approximation when modeling hydroxyl radical concentrations in a UV treatment reactor. An advanced oxidation model that was developed by Michigan Technological University researchers to assess the suitability of the steady-state assumption was evaluated as part of this study (Crittenden et al., 1999). The Crittenden model illustrates that the steady-state model approximation is satisfactory for highly treated recycled wastewater (i.e., RO effluent) which contains low concentrations of bicarbonate, carbonate, and hydroxide anions.

$$[OH\cdot]_{ss} = \frac{f_{H_2O_2}\phi_{H_2O_2}\left(\eta R_{eff}P \big/ N_{av}Vh\nu\right) + k_1[H_2O_2][HO_2\cdot]}{\sum_i k_i[Absorber]_i} \tag{9}$$

where

$[OH^{\cdot}]_{ss}$ = Steady-state concentration of hydroxyl radicals (mol L^{-1})
f_{H2O2} = Fraction of UV light absorbed by H_2O_2, calculated analogously to NDMA using eq 3 or 5 (unitless)
ϕ_{H2O2} = Quantum yield for H_2O_2, taken to be 1.0 (unitless) (MWH, 2005)
η = Electrical efficiency (unitless)
R_{eff} = Radiant efficiency (unitless)
P = Power supplied to UV reactor (W)
N_{av} = Avogadro's number, 6.02×10^{23} (photons einstein^{-1})
V = Reactor volume (L)
$h\nu$ = Planck's constant, $6.62 \times 10^{-34} \times$ UV light frequency (J)
k_1 = Rate constant for the reaction of H_2O_2 with HO_2 radicals, 3.5 L mol^{-1} s^{-1}
$[H_2O_2]$ = Concentration of H_2O_2 (mol L^{-1})
k_i = Pseudo-first-order rate constant for reaction of $^{\cdot}OH$ with organic compounds (low molecular weight carboxylic acids, ketones, aldehydes, etc.) (s^{-1})
[Absorbers] = Concentrations of organics that react with hydroxyl radicals (mol L^{-1})

Since the product of concentration and rate constant is small for radicals such as $HO_2^{\cdot}$ compared to the concentration and rate constant of H_2O_2, some of the terms in eq 9 can be neglected. The simplified equation is as follows:

$$[OH\cdot]_{ss} = \frac{f_{H_2O_2}\phi_{H_2O_2}\left(\eta R_{eff}P \big/ N_{av}Vh\nu\right)}{k_2[H_2O_2]} \tag{10}$$

where

k_2 = Rate constant for H_2O_2 reaction with $^{\cdot}OH$ (1.1×10^{10} L mol^{-1} s^{-1}) (Stefan et al., 1996)
$[H_2O_2]$ = Concentration of H_2O_2 (mol L^{-1})

Many of the same variables specified in the UV photolysis model can be used to determine the steady-state hydroxyl radical concentration. Using the reactor dimensions, flow rate, and water quality data from the OCWD demonstration study (reactor volume of approximately 29 gallons and flow rates ranging from 100 to 1000 gpm), the model predicted a steady-state hydroxyl radical concentration ranging from 4×10^{-12} to 9×10^{-12} mol/L at an H_2O_2 concentration of 5 mg/L.

Multiplying this by the second-order reaction rate constant that was previously calculated (1.3×10^{10} L mol^{-1} s^{-1}) resulted in a pseudo-first-order reaction rate that ranged from 0.052 to 0.12 s^{-1} (3 to 7 min^{-1}). Using the tanks-in-series model (eq 2), the removal rate of unknown organic compounds can be predicted as a function of residence time and H_2O_2 dose. Results are shown in Table 6-5.

Table 6-5. Model-Predicted Removal of Unknown Organic Compounds during Advanced Oxidation (H_2O_2 and UV)

Flow Rate, gpm	Residence Time, s	% Removal of Organics by Advanced Oxidation with UV and H_2O_2 at: 2 mg/L	5 mg/L	10 mg/L
100	17	39–48	62–80	77–96
500	3	12	25	39–48
1000	1.7	6	14	25–28

Note: The range of percent removal listed corresponds with the range of possible reactor hydraulic configurations (CMFR to PFR). Water quality was characterized by a UV transmittance of 96.6%.

As shown in Table 6-5, the predicted removal rate for unidentified organic compounds is poor at low H_2O_2 concentrations but improves as retention time and H_2O_2 dose increase. At 5 mg/L, removal rates ranging from 15 to 80% were predicted. This modeling exercise demonstrates H_2O_2 addition may significantly reduce concentrations of low molecular weight organic compounds if hydraulic retention times exceed 10 s. Peroxide addition may provide an additional measure of protection against uncharacterized organic compounds that survive RO treatment.

6.5 CONCLUSIONS

The water quality-based UV photolysis model presented in this chapter allows utilities to predict NDMA removal rates based on reactor size, hydraulic configuration, lamp power, and influent water quality. Utilities can use the model to estimate NDMA removal rates as a function of influent water quality. The cost of electricity during UV treatment of NDMA can be directly calculated using model-predicted EE/O values. A comparison of modeling results with demonstration-scale test data collected at OCWD suggests that the photolysis model accurately predicts the range of effluent NDMA concentrations on average. Modeling results could be compared with empirical data collected from a full-scale system as a follow-up study.

Several studies have found that NDMA removal is not improved by the addition of H_2O_2 during UV treatment unless high concentrations of peroxide (~50 mg/L) are added (Bolton, 2002; Modifi et al., 2000; Sharpless and Linden, 2003). The addition of H_2O_2 does not result in any quantifiable benefits for removing NDMA precursors, because NDMA precursors are well removed by RO. The advanced oxidation component of the UV modeling demonstrates potential benefits of adding H_2O_2 during UV treatment to oxidize unknown organic compounds that may persist after RO. Removal rates ranging from 15 to 80% were predicted for hydraulic residence times of 1.7 and 17 s in the demonstration-scale system tested at OCWD (5 mg/L of H_2O_2).

CHAPTER 7

FATE OF NDMA AND NDMA PRECURSORS IN NONPOTABLE WATER REUSE SYSTEMS

7.1 INTRODUCTION

As discussed in Chapters 2 and 4, NDMA can form when municipal wastewater effluent containing ammonia is disinfected with chlorine. NDMA also can be formed when free chlorine is used in the absence of ammonia, but the concentrations formed are typically more than an order of magnitude lower than if chloramines are present (Mitch and Sedlak, 2004). Under typical chloramination conditions, approximately 100 ng/L of NDMA will form in municipal wastewater (Chapter 3). To meet California Title 22 regulatory requirements and to prevent biological growth in the reclaimed water distribution system, wastewater effluent that is used for agriculture and landscaping is usually disinfected with higher doses than effluent that is recharged or discharged to surface waters. It is therefore possible that much higher concentrations of NDMA form in nonpotable water reuse systems. Regulatory agencies do not require nonpotable water reuse programs to meet drinking water guidelines because they assume that NDMA will undergo photolysis, dilution, or biotransformation before reaching the aquifer. Even if partial attenuation and dilution significantly reduced the concentration of NDMA in irrigation water, it is still possible that the residual NDMA from nonpotable water reuse systems could contaminate local groundwater supplies.

To address these issues, the project team conducted a preliminary assessment of NDMA concentrations in nonpotable water reuse systems and evaluated the potential for NDMA to form as a result of the additional disinfection applied in nonpotable reuse systems. The project team collected samples from several locations at six full-scale nonpotable water reuse facilities and performed laboratory studies to assess the kinetics of NDMA formation at chloramine doses typically applied in nonpotable water reuse systems.

7.2 MATERIALS AND METHODS

7.2.1 Materials

All chemicals used in the laboratory studies were analytical grade and were purchased from Fisher Scientific or Sigma-Aldrich. All laboratory glassware was washed with Nanopure water, rinsed with methanol, and baked for 4 h at 450°C prior to use. To avoid the possible introduction of NDMA or NDMA precursors into samples during the addition of chlorine or pH buffers, Fisher environmental-grade low-carbon water was used in the preparation of all laboratory solutions and reagents.

7.2.2 Sample Collection and Analysis

Samples were collected from the six wastewater treatment plants listed in Table 7-1. To maintain confidentiality of the results, treatment plants will be referred to as Systems 1 through 6. The treatment plants and distribution systems are representative of systems currently practicing nonpotable reuse for agriculture and landscape applications. Conventional activated sludge treatment is used for secondary wastewater treatment in these systems. All of the systems employed effluent filtration, and four of the six systems employed nitrification-denitrification.

Table 7-1. Characteristics of Nonpotable Water Reuse Systems

System	Design Capacity, m^3/s (MGD)	Advanced Treatment NDN?	Advanced Treatment Filtration?	Target Chlorine Dose,[a] mg-min/L	Target Residual Chlorine Concentration, mg/L
1	0.9 (20)	No	Yes	450	4
2	1.3 (30)	No	Yes	1200	23
3	0.7 (15)	Partial[b]	Yes	--	6
4	1.1 (25)	Yes	Yes	1200	5
5	0.3 (7)	Yes	Yes	840	9 (7–12)
6	7.0 (160)	Yes	Yes	--	7–10

[a] Dose is a product of the chlorine concentration and contact time.

[b] Nitrification is complete; however, 0.5 mg/L of ammonia is added prior to disinfection.

Treatment facilities ranged in size from 0.3 to 7 m^3/s (7 to 160 MGD). Typically, tertiary filtered effluent was disinfected in a chlorine contact tank where chlorine was applied in order to meet the target disinfectant dose. At System 2, treated wastewater entered a holding pond after chlorination but prior to entering the distribution system for nonpotable purposes.

Samples were collected before and after chlorine disinfection at the treatment plants and at one or more locations within the nonpotable water reuse distribution systems. Distribution system samples were typically grab samples collected in I-Chem 300 series 2-L amber glass bottles. At Systems 1 through 5, wastewater effluent was collected before and after chlorination in 24-h composite samples using refrigerated composite samplers equipped with Teflon-lined polypropylene containers. At System 4, polyethylene bottles were used. A duplicate sample collected from System 4 in a Teflon-lined container indicated that the polyethylene bottle did not affect the concentration of NDMA or NDMA precursors.

To quench chlorine residual and stop NDMA formation, 40 to 50 mg/L of sodium thiosulfate was added to the sample containers prior to sample collection. Free and combined chlorine was measured on separate aliquots of freshly collected samples immediately after collection by utility field technicians using the DPD colorimetric method (standard method 4500-Cl G). The utility laboratories analyzed wastewater samples for ammonia (method 4500-NH_3 C), nitrate (method 4500-NO_3^-), nitrite (method 4500-NO_2 B), total organic carbon (method 5310 B), and dissolved organic carbon (method 5310 C) (APHA, 1998).

Aliquots of samples from all locations were shipped overnight to the OCWD laboratory, where they were extracted and analyzed for NDMA and NDMA precursors using liquid-liquid extraction followed by chemical ionization, isotope dilution, and GC/MS. Total NDMA precursors were analyzed using the NDMA precursor test described in Chapter 2 and detailed by Mitch et al. (2003a).

7.2.3 Laboratory Studies of NDMA Formation Rates

Composite samples of secondary or tertiary effluent collected prior to chlorine disinfection were shipped overnight to UC Berkeley, where experiments were started within 72 h of the beginning of sample collection, except for the samples from Systems 2 and 3, which were stored at 4°C for up to 6 days prior to the start of the experiment. Upon arriving in the laboratory, the samples were decanted into glass containers and were chlorinated or chloraminated using initial chlorine concentrations of 0, 2.5, 5.0, and 10 mg/L of Cl_2. Samples from Systems 1 through 5 were chlorinated. The sample from System 5 also was chloraminated. Unchlorinated samples were also prepared as controls. To determine whether biodegradation of NDMA occurred in the control samples, 1 mM $HgCl_2$ was added to one of the two unchlorinated (control) samples. After adding chlorine, the samples were stored at room temperature in the dark.

Free chlorine (i.e., NaOCl) and monochloramine stock solutions (20 mM) were prepared daily. The chlorine stock solution was made by diluting Fisher brand 5% NaOCl solution. The monochloramine solution was prepared by adding concentrated NaOCl dropwise to a 22 mM solution of ammonium chloride (Mitch and Sedlak, 2002a). The pH of the monochloramine solution was adjusted to 8.0 prior to the addition of chlorine to minimize the formation of dichloramine. The total concentration of chlorine in each of the stock solutions was standardized in triplicate prior to initiating each experiment using iodometric titration (method 4500-Cl B) (APHA, 1998).

Separate aliquots from each treatment were sampled at different times. NDMA and total NDMA precursors were measured in the unchlorinated sample at the start of the experiment and at 50 h. The chlorinated treatments were sampled after 1, 10, and 50 h. The limit of quantification for the NDMA method was approximately 5 ng/L in the wastewater effluent matrix. Any chlorine remaining in the sample was quenched prior to extraction and NDMA analysis by adding 3.5 mL of 0.1 M $Na_2S_2O_3$.

Table 7-2. Summary of Laboratory Test Conditions

System	Nitrified?	Chlorine[a]	Chloramine[a]	None[b]	None ($HgCl_2$ Added)[b]
1	No	X		X	X
2	No	X		X	X
3	Yes	X		X	X
4	Yes	X		X	X
5	Yes	X	X	X	X

[a] Batch experiments were set up to test 0, 2.5, 5.0, and 10 mg/L of Cl_2. Chlorinated and chloraminated samples were analyzed after 1, 10, and 50 h.

[b] The two nonchlorinated samples served as controls. $HgCl_2$ was added to one of the samples to prevent biodegradation. Both samples were analyzed at the start of the experiment and after 50 h. There was no significant difference between NDMA concentrations in the two nonchlorinated samples, indicating that biodegradation did not occur in the samples over time.

NDMA was measured using solid-phase extraction followed by GC/MS/MS. The solid-phase extraction was performed with Ambersorb 572 (Supelco 10432-U) (Choi and Valentine, 2002; 2003). After spiking the solution with 10 µL of 2.5 ng/L of NDMA-d_6, approximately 0.25 g of Ambersorb beads was added to the sample. The sample was then stirred for at least 6 h with a magnetic stirrer or was placed on a shaker table. The beads were filtered (AP150900; Millipore Corp.) and air-dried for at least 12 h. The beads were extracted twice with 2 mL of methylene chloride and concentrated to 1 mL. The methylene chloride extract was analyzed on a Varian CP-3800 gas chromatograph coupled with a Saturn 2000 MS/MS (Mitch and Sedlak, 2002a).

7.3 OCCURRENCE STUDY RESULTS AND DISCUSSION

Results from sampling full-scale nonpotable water reuse systems indicate that NDMA is present in the irrigation water at concentrations ranging from less than 10 ng/L to approximately 600 ng/L. NDMA formation was related to the form of chlorine added for disinfection, the chlorine dose (chlorine concentration and retention time), and the concentration of NDMA precursors. Results from each system are presented in the following sections.

7.3.1 System 1

At System 1, samples were collected from the chlorinated final effluent and one location in the distribution system on May 25 and May 27, 2004. A sample was collected from filter effluent prior to chlorination on May 25, 2004. System 1 receives municipal wastewater effluent that has not been nitrified; chlorine added for disinfection is therefore converted into chloramines. The distribution system samples were collected from a location approximately 10 km from the treatment plant. Distribution system sample 1 was collected at 8:00 a.m., and distribution system sample 2 was collected at 2:00 p.m. During disinfection, concentrations of NDMA increased from approximately 50 ng/L to 400 ng/L. After disinfection, the concentration of NDMA remained relatively constant, with concentrations ranging from 330 ng/L to 520 ng/L in the six samples collected (Fig. 7-1).

System 1 is required to meet a total chlorine dose of 450 mg-min/L. In order to maintain the target concentration of 4 mg/L chlorine at the chlorine contact tank effluent, much higher concentrations of chlorine are applied. The high chlorine concentration, combined with ammonia concentrations ranging from 30 to 40 mg/L, forms NDMA within the chlorine contact basin. NDMA may continue to form in the distribution system; however, the retention time in the distribution system may not be long enough for residual chloramines to result in a measurable increase in NDMA concentrations from reactions of the remaining NDMA precursors, as shown in Figure 7-2.

The hydraulic residence time of these samples in the distribution system is unknown, but according to the operators of the system it ranges from 7 to 74 h, relative to the chlorine contact basin exit. On the basis of these estimates, the dose of chlorine received by the sample in the distribution system should have resulted in additional chloramine formation. Therefore, the absence of an increase in NDMA concentration within the distribution system also could have been related to the collection of grab samples from the distribution system.

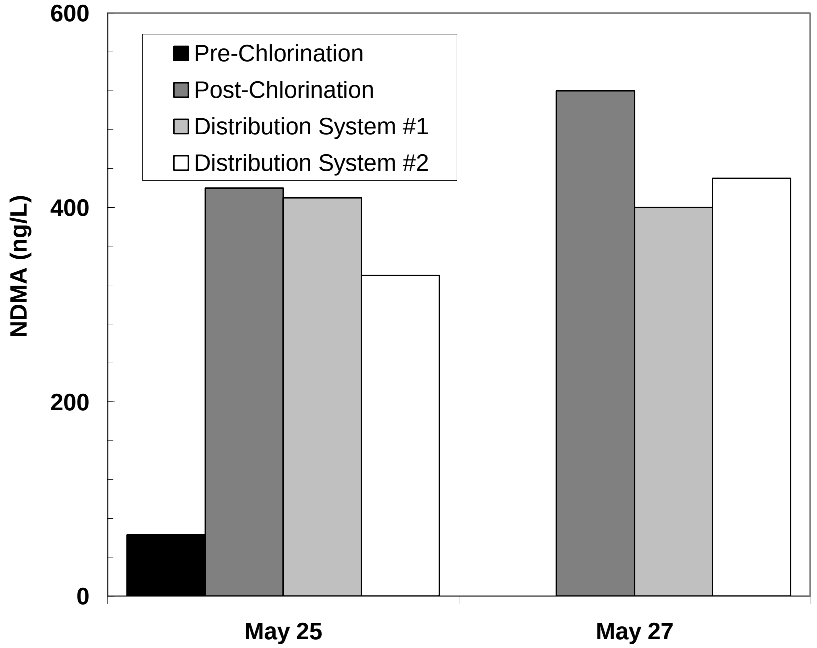


Figure 7-1. Concentrations of NDMA in System 1.

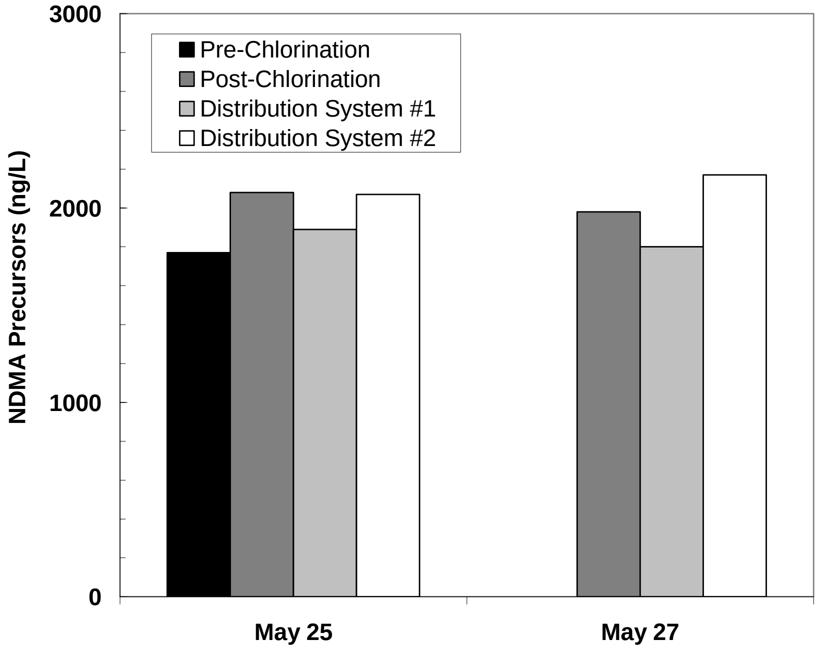


Figure 7-2. Concentrations of NDMA precursors in System 1.

As expected, concentrations of NDMA precursors remained approximately the same before and after chlorination. After subtracting the initial NDMA concentrations from the NDMA precursor test results, approximately 1800 ng/L–2100 ng/L of NDMA precursors remained in the treated wastewater effluent. This is in the upper range of NDMA precursor concentrations detected in wastewater effluent (Chapter 3). The relatively high concentration of NDMA precursors at this location contributes to the high NDMA formation rate after chloramination.

7.3.2 System 2

Samples were collected from the nonpotable water reuse system referred to as System 2 on Sept. 29, 2004. Like System 1, System 2 treats municipal wastewater effluent that has not been nitrified. Therefore, the free chlorine added during disinfection is converted into chloramines, making the system behave like a chloramination unit. Ammonia concentrations in System 2 ranged from 28 to 34 mg/L, while initial chlorine concentrations were approximately 23 mg/L. pH ranged from 7.8 to 8.1. Samples were collected before and after chlorine disinfection, from a holding pond that receives filtered chloraminated water, and from two locations in the distribution system.

The concentration of NDMA increased from approximately 25 ng/L prior to chlorination, to 100 ng/L at the exit of the chlorine contact basin, to approximately 250 ng/L in the pond. NDMA concentrations in the distribution system were approximately equal to those detected in the pond (Fig. 7-3).

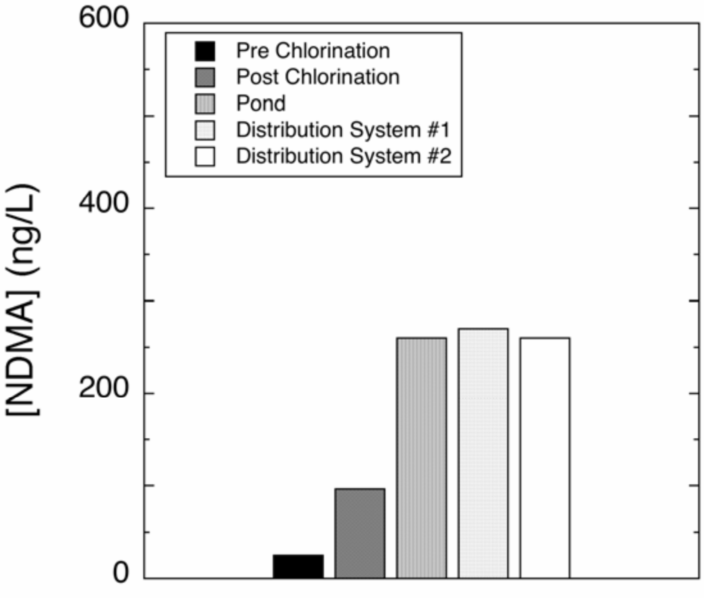


Figure 7-3. Concentrations of NDMA in System 2.

The increases of NDMA concentrations observed between the chlorine contact basin and the exit of the pond are consistent with the estimated chlorine doses at these two locations. The estimated cumulative chlorine contact dose is approximately 1200 mg-min/L at the chlorine contact basin and 8200 mg-min/L at the exit of the retention pond (the hydraulic retention time in the pond is approximately 15 h at a residual combined chlorine concentration of 7 mg/L of Cl_2). As was the case with System 1, a large chlorine concentration is applied and reacts with ammonia to form NDMA after chlorination. NDMA may continue to form in the distribution system; however, the retention time in the distribution system may not be long enough to yield measurable increases in NDMA from reactions with the remaining NDMA precursors. Distribution system sample 1 was collected from a location relatively close to the pond, with an estimated hydraulic residence time between 5 and 60 min. Distribution system sample 2 was collected relatively close to sample 1, with a hydraulic residence time of between 10 and 100 min relative to the pond. In both cases, the additional contact time with chlorine in the distribution system resulted in a relatively small increase in total chlorine dose compared to the chlorine contact tank effluent and holding pond.

After subtracting the initial NDMA concentration, NDMA precursor concentrations detected at System 2 ranged from approximately 400 ng/L to 1500 ng/L, as shown in Figure 7-4.

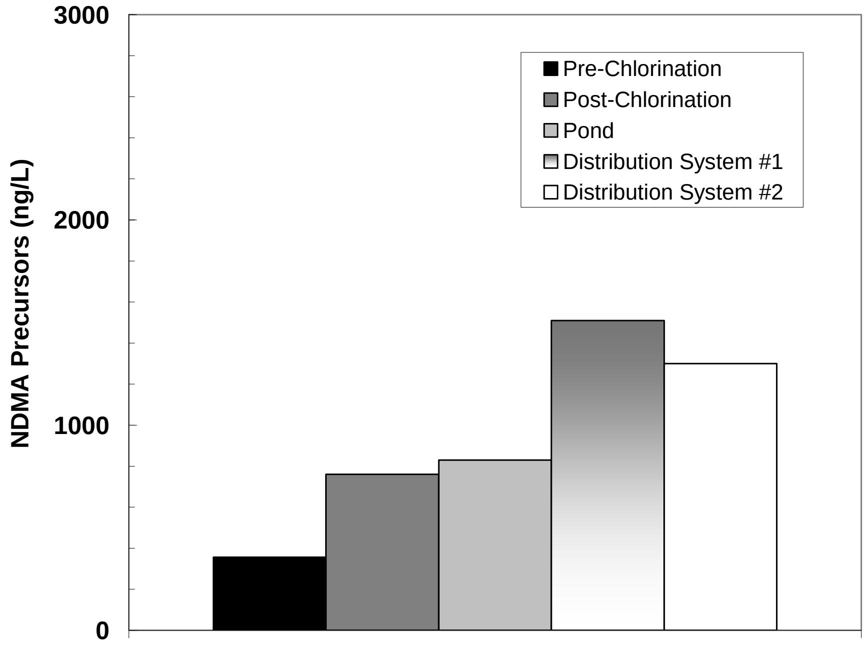


Figure 7-4. Concentrations of NDMA precursors in System 2.

The apparent increase in total NDMA precursors observed between prechlorination and postchlorination samples may be due to the fact that composite samplers were not staggered to collect the same water flowing through the plant. An apparent increase in NDMA precursors was also observed in the distribution system after irrigation water was left in the holding pond. However, the holding pond and distribution system sample results are from grab samples, which are less representative of a daily average concentration than the 24-h composite samples collected before and after chlorination.

As with System 1, NDMA precursors are in the upper range of NDMA precursor concentrations typically detected in wastewater effluent (Chapter 3). The magnitude of NDMA precursors contributes to NDMA formation upon chloramination.

7.3.3 System 3

Samples were collected from the nonpotable water reuse system referred to as System 3 on May 3 and July 13, 2004. System 3 treats municipal wastewater effluent that has been nitrified to reduce total nitrogen concentrations. After the effluent is nitrified, some ammonia is added immediately after free chlorine into the disinfection system. Thus, the chlorine is added as chloramines. The target ammonia concentration is 0.5 mg/L during chloramination to maintain a chloramine residual; laboratory results indicate ammonia levels ranging from 0.1 to 0.65 mg/L. Samples were collected before and after chlorine disinfection, at the start of the distribution system, and from a lake on a golf course where recycled water is applied. On May 3, 2004, two grab samples were collected from the distribution system, and on July 13, 2004, a 24-h composite sample was collected from the distribution system. Two grab samples were collected from the lake on both days. The lake is located approximately 2 miles from the treatment plant, and the estimated hydraulic residence time of the water in the system ranges from 18 to 24 h. The golf course uses only recycled water and, therefore, the water sampled from the lake consisted entirely of water that had been through the treatment system. The lake is situated at the upper end of the golf course; drainage from the surrounding turf is likely to be minimal except in storm events, which did not occur at the time of sampling.

Substantial NDMA formation was observed during chlorination in System 3. Between 100 and 400 ng/L of NDMA formed, similar to the increase observed in Systems 1 and 2. Concentrations prior to disinfection were below 50 ng/L in two samples (5 and 25 ng/L), which is consistent with several previous NDMA sample results collected at this facility. On one occasion, elevated (140 ng/L) NDMA concentrations were measured prior to chlorination (Fig. 7-5).

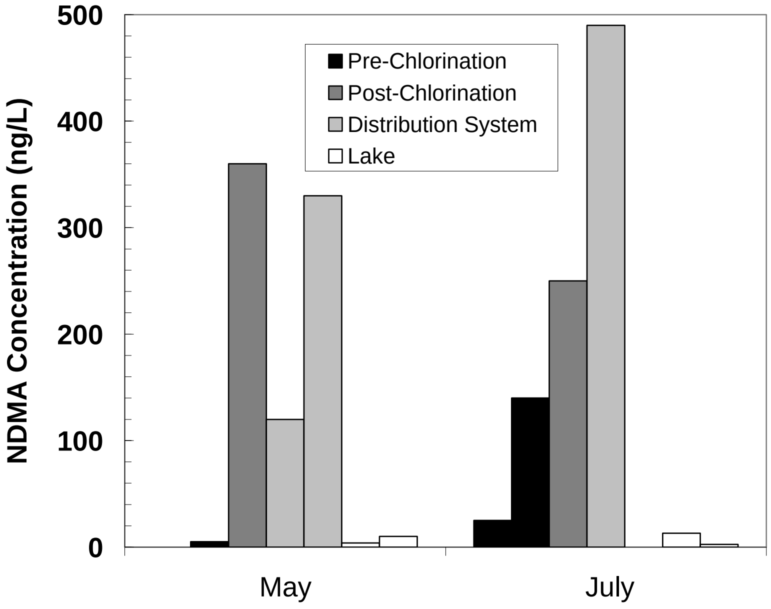


Figure 7-5. Concentrations of NDMA in System 3.

NDMA concentrations did not appear to consistently increase or decrease in the distribution system following chlorination. The mixed use of grab samples and composite samples makes it difficult to compare the results from postchlorination and the distribution system. During the May sampling event, concentrations appeared to decrease in the distribution system. During the July sampling event, concentrations appeared to increase in the distribution system. In general, concentrations ranged from 125 to 500 ng/L after chlorination. On both sampling days, NDMA concentrations in the lake were below 15 ng/L, despite concentrations at least an order of magnitude higher than this at the start of the distribution system. Although NDMA photolysis is the most likely destruction mechanism for water in the lake, the timing of the grab sample collection (one sample collected at mid-day in full sun and the other collected in the early morning) did not significantly affect results. The residence time in the lake is long enough to dilute incoming treated wastewater with the existing lake water. The low concentrations of NDMA in the lake are consistent with the relatively fast sunlight photolysis of NDMA (i.e., half-life on the order of an hour near the surface of the lake under mid-day sun).

The concentrations of NDMA precursors at the treatment plant and in the distribution system ranged between approximately 200 and 1200 ng/L (after subtracting initial NDMA concentrations) with no obvious trend between locations (Fig. 7-6). The concentration of NDMA precursors measured in the lake water samples was approximately half of the concentration measured in other parts of the system, suggesting that biodegradation or photolysis of NDMA precursors may occur in the lake.

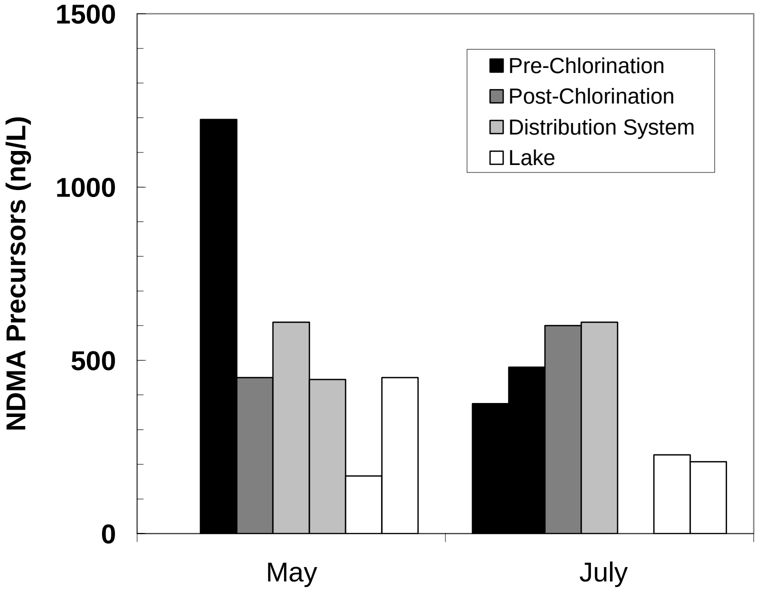


Figure 7-6. Concentrations of NDMA precursors in System 3.

7.3.4 System 4

Samples were collected from the nonpotable water reuse system referred to as System 4 on June 28, 2004. System 4 treats municipal wastewater effluent that has been nitrified prior to disinfection. Confirmatory samples analyzed for ammonia all indicated the absence of ammonia (i.e., <0.1 mg/L). The chlorine disinfection system employs free chlorine. pH ranged from 7.5 to 7.6. Samples were collected before and after chlorine disinfection and from one location in the distribution system. Both a 24-h composite sample (distribution sample 1) and a grab sample (distribution sample 2) were collected from the distribution system. The estimated hydraulic retention time between the chlorine contact basin and distribution sample location ranged from 4 to 48 h depending on irrigation practices. Distribution sample 2 was collected after water had been sitting in the distribution system for approximately 8 h following nighttime irrigation.

The concentration of NDMA increased from 100 ng/L to approximately 250 ng/L during the chlorination process and then decreased within the distribution system back to concentrations comparable to those detected prior to chlorination (Fig. 7-7).

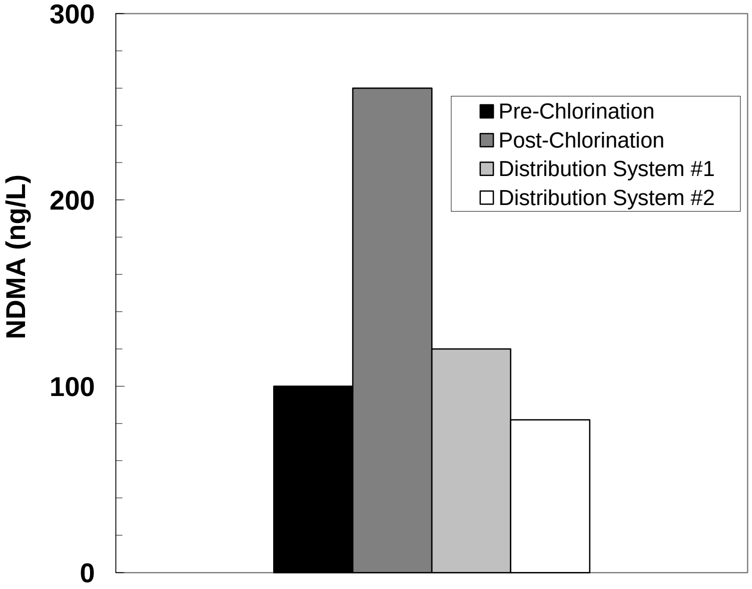


Figure 7-7. Concentrations of NDMA in System 4.

The formation of NDMA during chlorination and subsequent decrease in NDMA concentrations between the chlorination system and the distribution system were unexpected. There is no evidence suggesting that significant losses of NDMA occur in distribution systems. The apparent discrepancy could be related to the timing of the composite samples, since the samples were not staggered to collect the same flow of water through the system. The concentration of NDMA precursors remained relatively low throughout System 4, ranging from approximately 250 ng/L to 400 ng/L, after subtracting initial NDMA concentrations (Fig. 7-8).

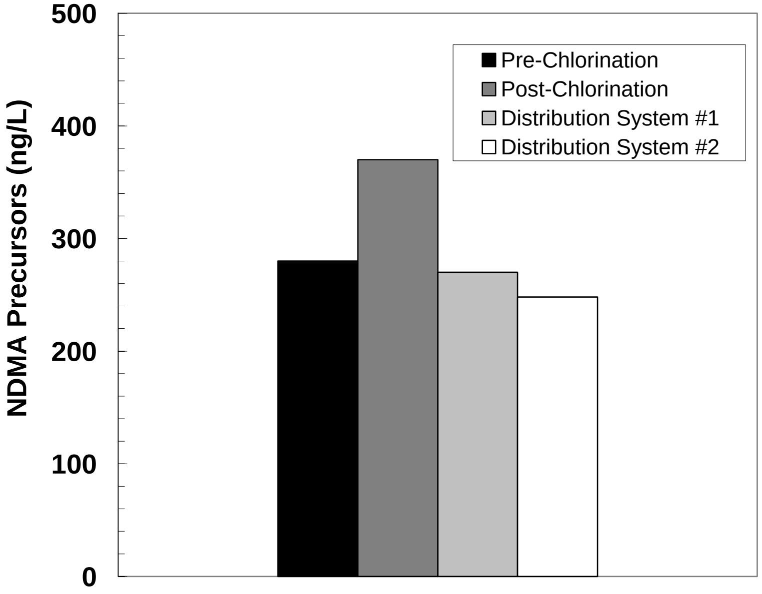


Figure 7-8. Concentrations of NDMA precursors in System 4.

7.3.5 System 5

Samples were collected from System 5 on Aug. 10 and 11, 2004. System 5 treats municipal wastewater effluent that has been nitrified prior to disinfection (ammonia concentrations were <0.1 mg/L). Therefore, the chlorine disinfection system employs free chlorine. pH was measured as 7.7 in secondary effluent. Twenty-four-hour composite samples were collected before and after chlorine disinfection. Grab samples were collected from a location in the distribution system at 8:00 a.m. and 2:00 p.m. The estimated hydraulic retention time of the samples was not available.

The concentration of NDMA was below 10 ng/L in all samples except for the second sample from the distribution system, which contained 910 ng/L of NDMA (Fig. 7-9). The sample with the anomalously high concentration of NDMA was reanalyzed, and the high concentration of NDMA was confirmed. The high concentration of NDMA was unexpected, because the concentrations measured after disinfection and in the other distribution system samples were low. According to laboratory personnel at the Orange County Water District, the labels on the sample containers were not intact, and it is possible that the sample was mislabeled. However, no other samples with such high concentrations of NDMA were detected in this batch of samples. The sample may have been contaminated during sampling.

The concentration of NDMA precursors in the samples from System 5 ranged from approximately 70 to 350 ng/L, after subtracting initial NDMA concentrations (Fig. 7-10). The concentrations of NDMA precursors in the 24-h composite samples collected before and after disinfection were similar. The four grab samples collected from the distribution system were also similar but contained lower concentrations of NDMA precursors.

Both Systems 4 and 5 contained much lower NDMA precursor concentrations than Systems 1 through 3. NDMA precursors were less than 100 ng/L in System 4 and less than 50 ng/L in

System 5. In contrast, Systems 3 through 5 contained 500 to 1000 ng/L, 1000 to 2000 ng/L, and approximately 2000 ng/L NDMA precursors, respectively. The low levels of NDMA precursors and the lack of ammonia present during disinfection result in low NDMA formation.

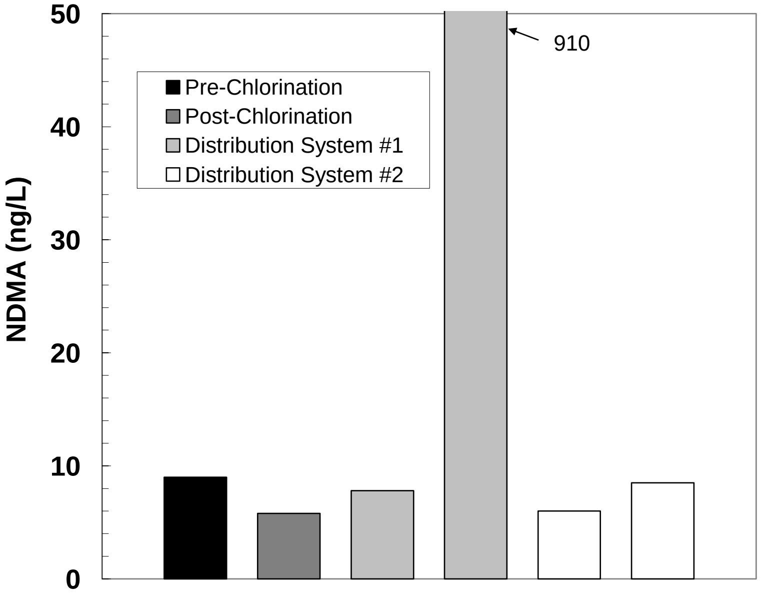


Figure 7-9. Concentrations of NDMA in System 5.

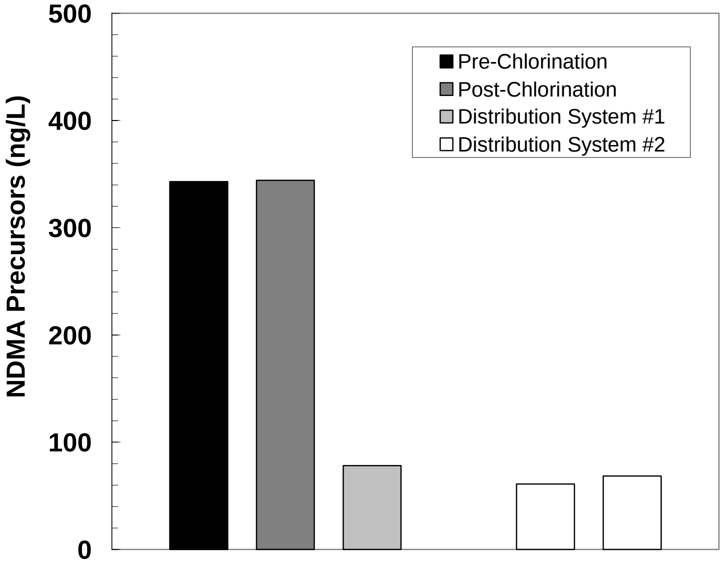


Figure 7-10. Concentrations of NDMA precursors in System 5.

7.3.6 System 6

Like Systems 3 through 5, System 6 also treats municipal wastewater effluent that has been nitrified prior to disinfection. Therefore, the chlorine disinfection system employs free chlorine. Grab samples were collected on May 10, 2004, from a point in the distribution system that is approximately 20 km from the chlorine contact basin and from an intermediate pump station located in the distribution system approximately 25 km from the chlorine contact basin. The reported hydraulic residence time after the chlorine contact basin ranges from 12 h to a few days.

Samples were not collected from before and after chlorination during the May sampling event; however, previous samples collected at this facility indicated that secondary effluent ranged from 18 to 70 ng/L of NDMA prior to chlorination and from 15 to 26 ng/L of NDMA after chlorination. The concentration of NDMA in the samples collected from the non-potable water reuse system ranged from 25 to 50 ng/L (Fig. 7-11). We do not have an explanation for the slight decrease in NDMA concentrations observed after chlorination. The concentration of NDMA measured at the pump station was similar to the concentration detected immediately after disinfection at the treatment plant and those collected in the distribution system.

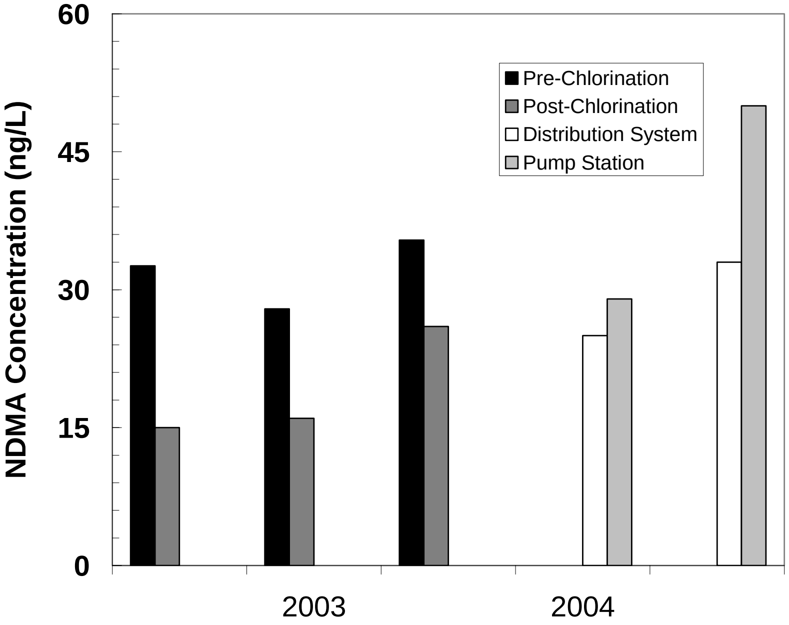


Figure 7-11. Concentrations of NDMA in System 6.

After subtracting initial NDMA concentrations, the concentration of NDMA precursors in the samples from System 6 ranged from approximately 140 to 430 ng/L. This is lower than levels of NDMA precursors detected in secondary effluent at this facility in 2003, as shown in Figure 7-12.

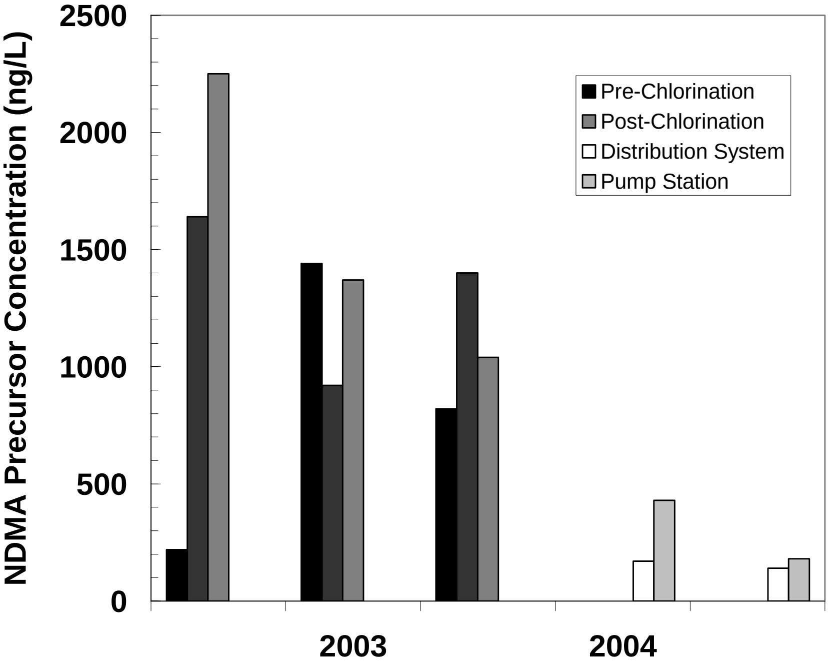


Figure 7-12. Concentrations of NDMA precursors in System 6.

7.3.7 Comparison of System Results

The most important variable affecting the concentration of NDMA in the nonpotable water systems sampled in this preliminary study was the form of chlorine applied during disinfection. The median concentration of NDMA formed during disinfection in systems using chloramines was 340 ng/L, compared to a median of less than 10 ng/L in systems where free chlorine acted as the disinfectant. This is a significant increase, considering that the median concentration of NDMA in wastewater effluent prior to disinfection was 46 ng/L with a maximum concentration of 380 ng/L (Chapter 3).

In systems using chloramines as a disinfectant, a relationship was observed between the concentration of NDMA formed in the disinfection system and the concentration of total NDMA precursors, as indicated by the filled symbols in Figure 7-13.

A qualitative relationship was observed between the chlorine dose and NDMA formation in the full-scale treatment systems. For example, in System 2, the concentration of NDMA increased by approximately 75 ng/L as the water passed through the chlorine contact basin. The concentration of NDMA continued to increase by an additional 160 ng/L between the chlorine contact basin and the outlet of the storage pond. The estimated chlorine dose at the end of the chlorine contact basin was 1200 mg-min/L, whereas the estimated dose was 7000 mg-min/L between the chlorine contact basin and the outlet of the pond.

On the basis of this relationship, it appears that 10–20% of the total NDMA precursors were converted to NDMA in the chlorine disinfection systems studied when treating nonnitrified effluents. This is higher than results measured under conventional municipal wastewater disinfection conditions. For example, at Los Angeles County Sanitation District’s Whittier Narrows treatment facility, approximately 5% of the NDMA precursors were converted into NDMA during disinfection (Chapter 3) (Sedlak et al., 2005).

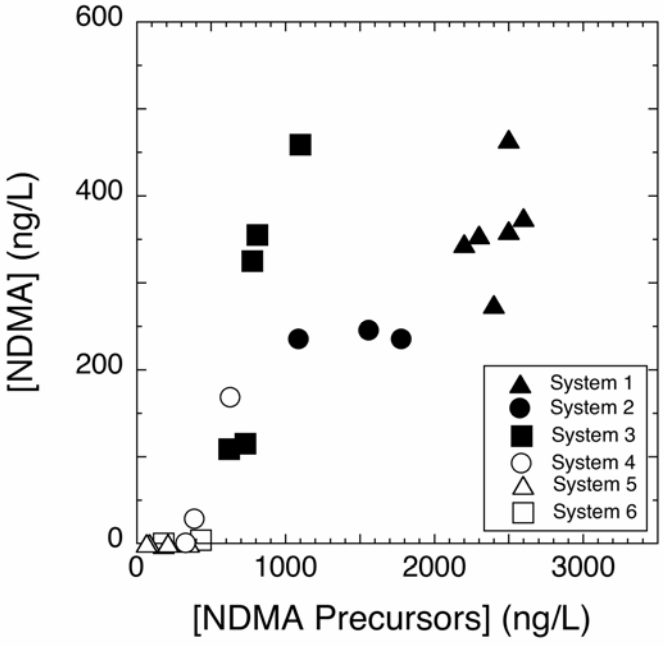


Figure 7-13. Correlation between NDMA concentrations observed after disinfection and total NDMA precursor concentrations in full-scale nonpotable water reuse systems. Systems using free chlorine are designated by hollow symbols, and systems using inorganic chloramines are designated by filled symbols.

7.4 LABORATORY STUDY RESULTS AND DISCUSSION

To build on the full-scale sampling results and previous research indicating higher NDMA formation at plants that chloraminate (Mitch and Sedlak, 2004), the project team conducted laboratory studies to examine the kinetics of NDMA formation during chlorination or chloramination and to illuminate the relationship between chlorine dose (chlorine concentration and contact time) and NDMA formation. Composite samples of nonchlorinated secondary or tertiary effluent were collected from Systems 1 through 5. The results are presented in the following sections.

7.4.1 System 1

Tertiary (postfiltration) wastewater effluent collected prior to chlorination from System 1 was treated with NaOCl. The wastewater effluent already contained 36 mg/L of NH_3 as N (i.e., 2.6 mM), which is approximately an order of magnitude higher than the highest concentration of chlorine applied (i.e., 0.29 mM). Therefore, most of the applied chlorine was converted into inorganic chloramines.

NDMA formed at all three chlorine concentrations used in the laboratory study. At chlorine levels of 5 and 10 mg/L, approximately 1000 and 1800 ng/L of NDMA was formed, respectively, over the 50-h experiment (Fig. 7-14). For comparison, the total NDMA precursor concentration measured in this sample prior to chlorine addition was 1200 ng/L.

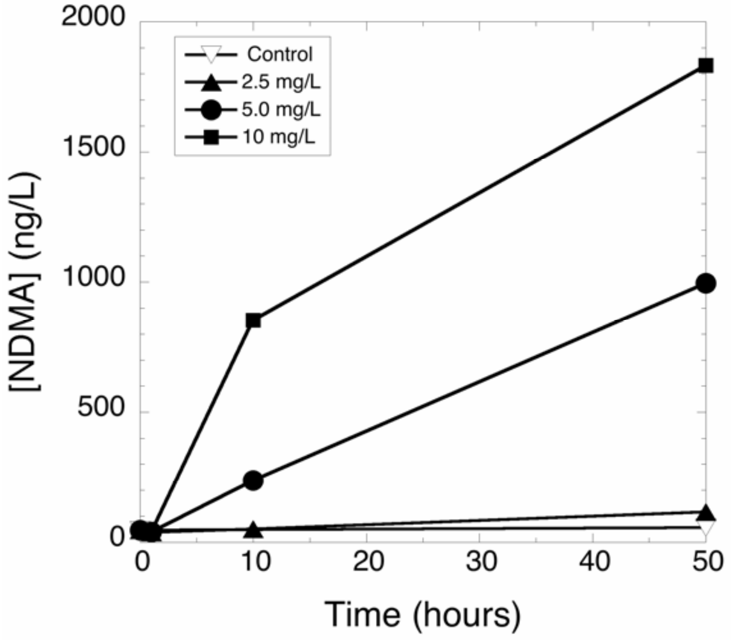


Figure 7-14. Formation of NDMA in System 1 wastewater during laboratory chlorination experiments in the presence of 0, 2.5, 5.0, and 10 mg/L of chlorine.

By multiplying each chlorine concentration by the contact time, the total chlorine dose was obtained. Laboratory results could then be presented in terms of NDMA formation at different total chlorine doses, enabling a comparison of laboratory data with full-scale data collected from the System 1 distribution system. As shown in Figure 7-15, NDMA formation is well-correlated with total chlorine dose.

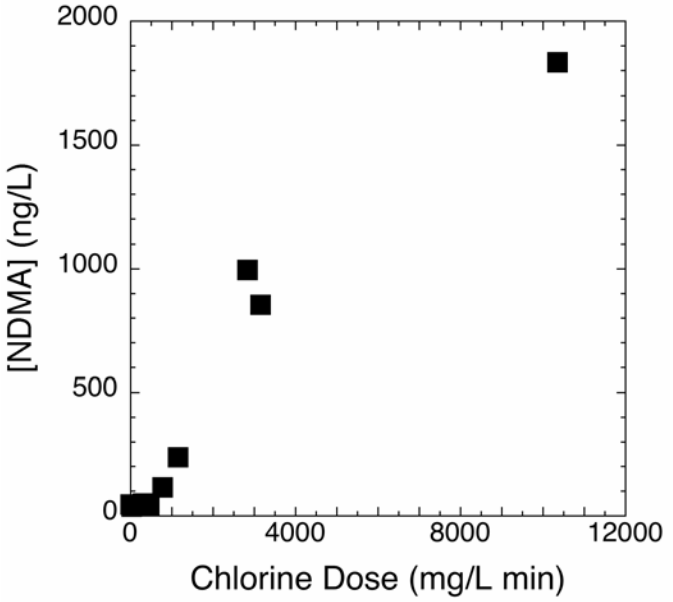


Figure 7-15. Formation of NDMA in System 1 wastewater as a function of chlorine dose.

Applying these results to field measurements of NDMA in System 1 following chlorination shows that the NDMA measured in System 1 (approximately 400 ng/L) could have formed by applying a chlorine dose of 1000 mg-min/L. While this dose is higher than the minimum target dose required in System 1's permit (450 mg-min/L), it is well within the range of chlorine doses required in practice in nonpotable water reuse systems to maintain an acceptable chlorine residual in the distribution system.

7.4.2 System 2

To assess NDMA formation in System 2, kinetic studies were conducted by adding free chlorine to secondary effluent samples. Results of the kinetic study indicated little formation of NDMA at any of the chlorine concentrations (Fig. 7-16). The absence of NDMA formation is inconsistent with results obtained at the full-scale treatment system (i.e., Fig. 7-3), where approximately 75 ng/L of NDMA formed in the chlorine contact basin and 150 mg/L of NDMA formed between the wastewater effluent and the pond outlet.

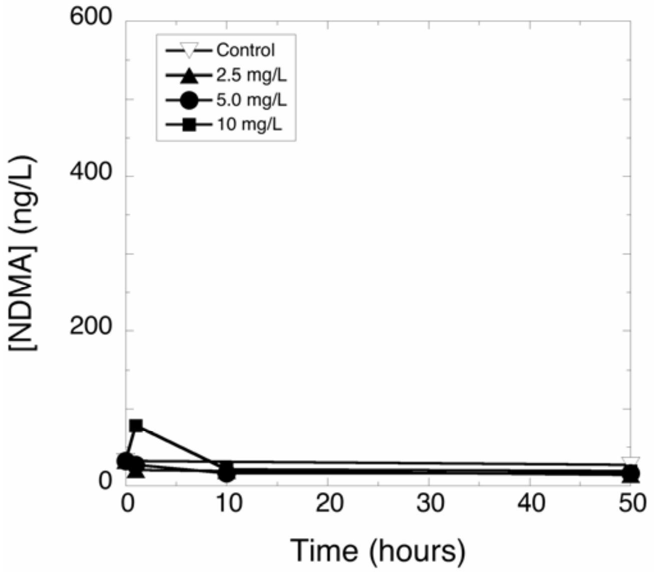


Figure 7-16. Formation of NDMA in laboratory chlorination experiments at System 2 in the presence of 0, 2.5, 5.0, and 10 mg/L of chlorine.

Total NDMA precursor concentration measured in this sample was 390 ng/L, compared to concentrations ranging between 750 ng/L and 1500 ng/L in other samples collected from the full-scale system. Therefore, the lower-than-expected formation of NDMA could have been related to the relatively low concentration of NDMA precursors in this sample. Alternatively, some of the ammonia may have been lost during the three-day delay between sample collection and the initiation of the experiment.

7.4.3 System 3

Free chlorine (NaOCl) was also added to secondary effluent collected from System 3. Due to a shipping error, the experiments were started 6 days after the start of the sample collection.

The sample contained 0.1 mg/L of NH_3 as N (i.e., 0.007 mM NH_3). Under these conditions, the ammonia in the sample should have been removed readily via breakpoint chlorination. It is possible that the lowest chlorine concentration did not pass the break point (i.e., 0.011 mM free chlorine) because some of the added chlorine would have reacted with solutes such as organic nitrogen prior to undergoing breakpoint reactions.

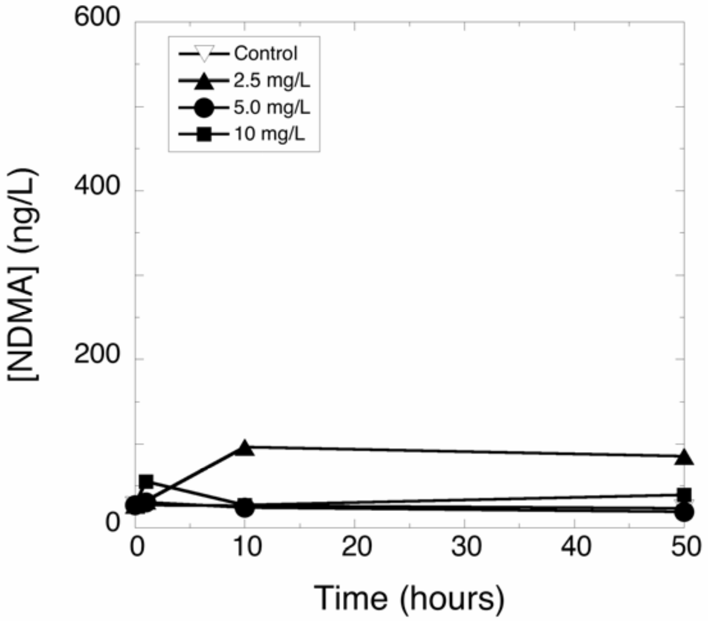


Figure 7-17. Formation of NDMA in laboratory chlorination experiments at System 3 in the presence of 0, 2.5, 5.0, and 10 mg/L of chlorine.

As expected, despite a high NDMA precursor concentration (400 ng/L), the data from System 3 indicate little to no formation of NDMA (Fig. 7-17). No NDMA formation was observed at 5.0 or 10 mg/L of chlorine. Approximately 80 ng/L of NDMA formed when 2.5 mg/L of chlorine was applied. It is possible that the ammonia or an inorganic chloramine species persisted at the lowest chlorine concentration but not at the higher chlorine concentrations, because the sample also contained organic nitrogen and other species that react with free chlorine. In general, the low levels of ammonia present in the wastewater kept NDMA from forming at the high concentrations seen in Systems 1 and 2.

7.4.4 System 4

Similar to System 3, NDMA did not form when NaOCl was added to a sample of tertiary (postfiltration) wastewater effluent collected from System 4. The sample used in this experiment did not contain any ammonia, and the lack of formation of NDMA is consistent with our expectations (Fig. 7-18).

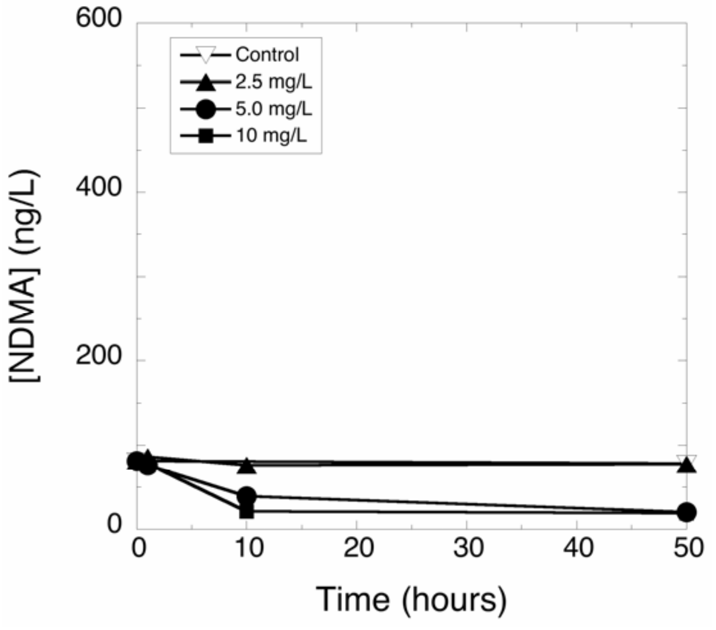


Figure 7-18. Formation of NDMA in laboratory chlorination experiments at System 4 in the presence of 0, 2.5, 5.0, and 10 mg/L of chlorine.

At higher chlorine concentrations (5.0 and 10 mg/L of Cl_2), NDMA concentrations may have decreased slightly. Full-scale data collected from System 4 indicate an apparent decrease in NDMA concentrations between the chlorination system and the distribution system. Since there is no evidence suggesting that significant losses of NDMA occur in the distribution system, follow-up studies should be conducted to confirm these results prior to concluding that NDMA is actually removed at high chlorine concentrations. Biodegradation was not likely to have occurred in the sample, since there was no decrease in NDMA concentration after 50 h in the two control samples (one treated with $HgCl_2$ to prevent biological growth) and it is unlikely that bacteria could survive at these high chlorine concentrations.

7.4.5 System 5

Two sets of tests were performed using a composite sample of denitrified secondary effluent from System 5 collected prior to disinfection. Like System 4, System 5 effluent is completely nitrified (ammonia, <0.1 mg/L). In the first experiment, chlorine was applied as NaOCl. As expected, little to no NDMA formed (Fig. 7-19).

In the second set of experiments, preformed monochloramine (NH_2Cl) was added at the same initial concentrations as NaOCl. As expected, significantly more NDMA formation was observed (Fig. 7-20). After 50 h of contact time, the different monochloramine treatments (0, 2.5, 5.0, and 10 mg/L of Cl_2) resulted in NDMA formation of 9, 20, 127, and 296 ng/L, respectively. At 10 mg/L for 50 h, NDMA formation approached that of the NDMA precursor test, 350 ng/L (i.e., the precursors were completely converted into NDMA at high chloramine concentrations).

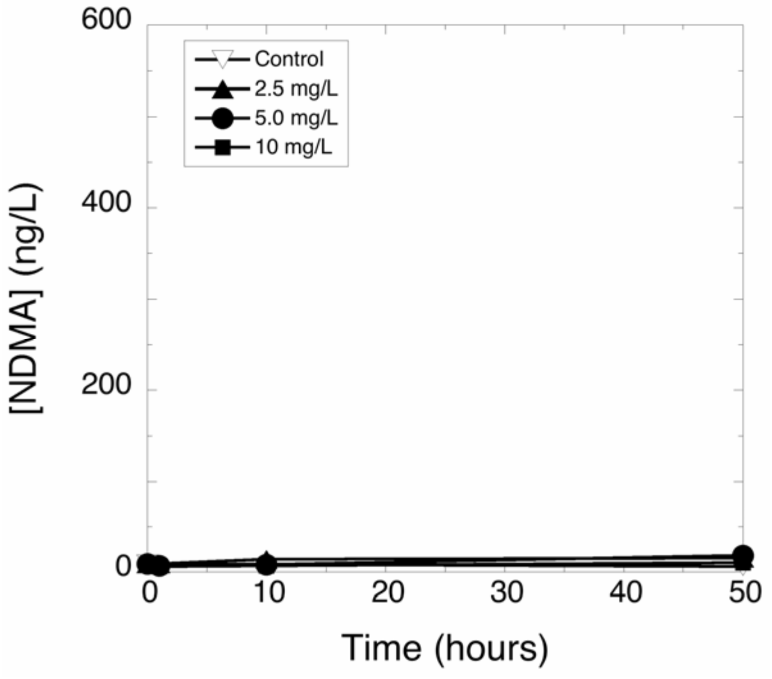


Figure 7-19. Formation of NDMA in laboratory chlorination experiments at System 5 in the presence of 0, 2.5, 5.0, and 10 mg/L of chlorine.

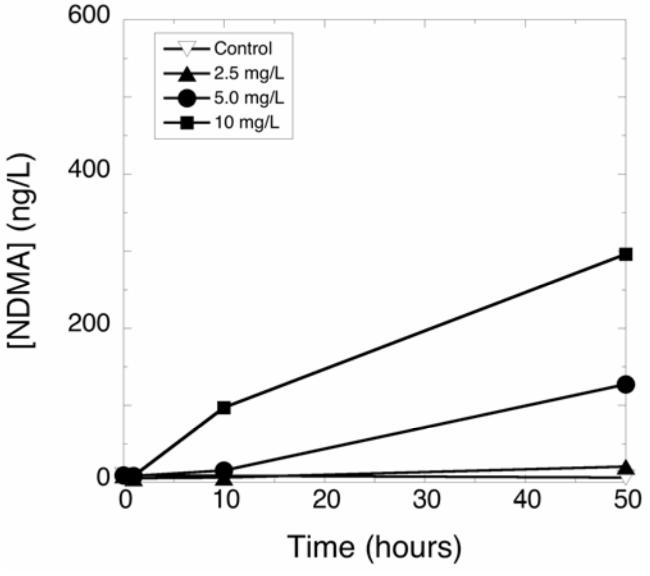


Figure 7-20. Formation of NDMA in laboratory chloramination experiments at System 5 in the presence of 0, 2.5, 5.0, and 10 mg/L of chloramines.

As with kinetics data from System 1, the chlorine concentration and reaction time were converted to a chloramine dose. A consistent relationship was observed between total chloramine dose and NDMA formation in the presence of ammonia (Fig. 7-21).

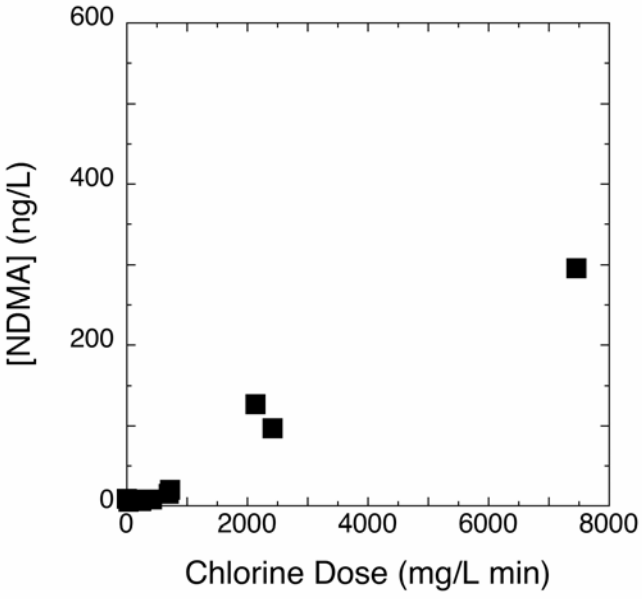


Figure 7-21. Formation of NDMA in System 5 wastewater as a function of chlorine dose.

The data illustrate that if in System 5 preformed monochloramines were added for disinfection, instead of free chlorine, at an average concentration of 10 mg/L of Cl_2 for 90 min, approximately 50 ng/L of NDMA would form in the chlorine contact basin. Using free chlorine, actual full-scale measurements of NDMA in treatment plant effluent were typically below 10 ng/L. If NDMA precursors were higher (similar to System 1), approximately 150 ng/L of NDMA could have been formed, as shown in Figure 7-15.

7.4.6 Comparison of Laboratory Results

Laboratory experiments performed using wastewater from five different nonpotable reuse systems confirmed a relationship between chlorine dose and NDMA formation. Results of the two experiments in which significant levels of NDMA formed upon chloramination (Systems 1 and 5) indicated a linear relationship between chloramine dose and NDMA formation (Fig. 7-15 and 7-21), although the rate of formation (slope) was different at the two sites, probably due to the variation in concentrations of NDMA precursors present in Systems 1 and 5. Under the conditions typically employed in nonpotable water reuse programs, increasing the chlorine dose (concentration or reaction time) should increase the concentration of NDMA formed, provided that excess ammonia is available.

7.5 CONCLUSIONS

The preliminary sampling and laboratory study described in this chapter indicates several approaches that may be useful for controlling NDMA concentrations in nonpotable water reuse systems:

- Implement nitrification to reduce ammonia concentrations prior to chlorination (i.e., practice chlorination, not chloramination).
- Reduce the dose of chlorine used during disinfection to the maximum extent possible, provided that microbial targets are being met.
- Lower NDMA precursor concentrations prior to disinfection by using advanced treatment, such as reverse osmosis.
- Use a process other than chlorination for disinfection, such as UV treatment.

Results of this study have shown that nonpotable water reuse systems that practice nitrification have significantly lower levels of NDMA in treated wastewater effluent, potentially below the California drinking water advisory level of 10 ng/L. In the three systems in which nitrified wastewater effluent was used, little if any NDMA formation was observed in the treatment system or in the laboratory studies. In these systems, the concentration of NDMA will be determined by the concentration in the wastewater effluent prior to disinfection (see Chapter 4). Other systems that disinfect with high levels of chloramines can form average NDMA concentrations of approximately 400 ng/L over a 24-h period, particularly when NDMA precursor concentrations are high (greater than 1000 ng/L).

As indicated by the results depicted in Figures 7-15 and 7-21 and by previous studies (Mitch and Sedlak, 2004), the dose of chloramines is linearly related to NDMA formation during disinfection. Although we did not collect enough data to predict the concentration of NDMA formed as the dose of chlorine increases, it should be possible to predict the magnitude of this increase by performing laboratory experiments, such as those described in this chapter, using samples collected from the treatment systems of interest.

The concentration of NDMA that formed in the disinfection systems was related to the concentration of NDMA precursors, particularly under chloramination conditions. As shown in Figure 7-13, systems with higher NDMA precursor concentrations resulted in more NDMA formation during chloramination. Under the chlorination conditions present in the nonpotable reuse systems sampled in this preliminary study, approximately 10–20% of NDMA precursors were converted to NDMA during chlorination.

An alternative approach for minimizing the concentration of NDMA in nonpotable water reuse systems involves a combination of UV disinfection and a lower concentration of chlorine to serve as a residual disinfectant in the distribution system. Unlike chlorine disinfection systems, UV treatment systems will not result in the production of NDMA. Furthermore, the UV radiation typically employed in nonpotable water reuse systems for disinfection might result in partial degradation of some of the NDMA. Additional research is needed to evaluate the potential for formation of NDMA by addition of residual chlorine.

CHAPTER 8

SUMMARY, CONCLUSIONS, AND STRATEGIES FOR UTILITIES TO CONTROL NDMA

8.1 FRAMEWORK FOR ADDRESSING NDMA AND OTHER EMERGING WATER QUALITY CONTAMINANTS

Wastewater utilities practicing water reuse face several issues raised by new and emerging water quality contaminants such as NDMA. How should utilities best prepare for upcoming water quality regulations? In light of the continual development of new compounds and new regulations, even if water quality currently meets drinking water standards, how can utilities ensure that delivered water is safe? Utilities must evaluate the threat of unregulated chemicals and make decisions as to the level of treatment required to address current and future threats.

When intentional indirect potable reuse first began, there were very few analytical methods to characterize wastewater organic content beyond bulk quantification methods, such as chemical or biochemical oxygen demand (Parkhurst, 1963). The benefits of water reclamation were presumed to outweigh the uncertainties. Two decades later, a treatment plant using water from the Potomac River and secondary nitrified effluent was found to produce effluent that was at least equal to the quality of the drinking water provided in the Washington, DC area (J. M. Montgomery, 1983). A subsequent review of this study by the National Academy of Sciences confirmed these results but concluded that less than 1% total organic carbon and less than 10% total organic halides had been identified; thus, this water was not necessarily of potable quality (i.e., the uncertainties exceeded the potential benefits of using this water for potable use).

Today, the fate and treatability of many organic chemicals with potential health concerns are better understood (e.g., Reinhard et al., 1986). Full-scale indirect potable reuse facilities incorporate advanced treatment, such as GAC and RO membranes. These facilities continue to produce effluent that meets and surpasses drinking water regulations. However, recent studies of NDMA in chlorinated wastewater effluent illustrate that the current level of treatment is not always sufficient to address future water quality threats. Additional treatment (i.e., UV treatment) has been added at these facilities to meet NDMA effluent requirements. A full accounting of all potential chemicals is still lacking, leaving utilities to apply their own safeguards for the future.

8.1.1 Current Regulatory Standards

The problem of emerging and unregulated chemical contaminants is not new to the regulatory community (NRC, 1977). In general, the current federal standards have evolved by continually addressing emerging contaminants. Initially, water quality standards were established for microbial contaminants and several inorganic contaminants, such as heavy metals. Prior to 1970, the detergent alkyl benzene sulfonate was the only organic chemical regulated in drinking water by the U.S. Public Health Service (0.5 mg/L). With the passage of the Safe Drinking Water Act in 1974, the federal government expanded the organic standards to include six pesticides. By 1986, the number of organic compounds regulated in drinking water had risen to 10, along with four trihalomethanes and six chlorinated volatile organic chemicals. There are currently (as of 2005) primary drinking water standards (MCLs) for 53 organic compounds. In addition, the 1996 Safe Drinking Water Act Amendments require the U.S. EPA to review at least five new contaminants every five years to determine whether or not they should be regulated. This has lead to the development of a Contaminant Candidate List, which currently includes 42 chemical contaminants and nine microbial agents.

8.1.2 Supplemental Regulatory Approach

Despite these efforts to keep pace with the detection of new contaminants, contaminant regulation is a slow process. Over the next two decades, no more than 10 contaminants are likely to be regulated at the federal level. In contrast, the reported number of chemicals in the world registered by the Chemical Abstracts Service exceeds 20 million. Of these, the U.S. EPA considers approximately 227,000 to be potential chemical contaminants (CHEMLIST, 2002). Approximately 3,000 are produced at levels exceeding 10,000 lb/year (U.S. EPA, 2002). NDMA and other emerging contaminants (e.g., perchlorate, MTBE, TBA, pharmaceuticals, and personal care products) suggest that using a standard-setting approach alone to ensure the safety of the drinking water supply may not be adequate to provide sufficient protection for human health.

State agencies have already begun using a more comprehensive approach with policies to protect human health. Many states have expanded their watershed protection programs, including Connecticut, which has recently imposed land use controls prohibiting the development of high-risk land use activities (e.g., dry cleaners, gas stations, manufacturing companies that use hazardous materials, landfills, and major petroleum storage facilities) in and around the state’s active well fields. The California DHS has developed a permit process to address “extremely impaired” potential water supplies (Spath, 1997). The policy includes requirements for assessing the occurrence of unregulated contaminants.

8.1.3 Implications for Utilities

Emerging contaminants such as NDMA raise a number of questions for utilities regarding allocation of responsibility for alleged impacts on human health. Recently, in the Hartwell decision in California, the Superior Court ruled that a water utility could not be held liable for alleged damages to consumers if the water met all appropriate drinking water standards established by public health agencies at the state level (Hartwell, 2002). The Court also ruled that current standards are adequate for protection of the public health but left unresolved any liability associated with exposure to unregulated or emerging contaminants. Legal issues remain uncertain, and the burden of risk management remains with the regulated utilities.

Under current regulations, the majority of utilities in the United States are not required to address NDMA. Utilities subject to California Department of Health Services’ Draft Groundwater Recharge and Reuse Requirements may be required to monitor for NDMA and potentially implement UV treatment in the near future. Utilities that decide to address unregulated contaminants through watershed protection efforts and advanced treatment should be aware that some unregulated compounds, like NDMA, form within the treatment plant and are not well-removed by traditional water treatment technologies (e.g., activated sludge, GAC, RO). Since a combination of several factors may determine how a utility responds to NDMA, water quality professionals should keep in mind that utilities face a number of water quality regulations, emerging contaminants, and operational constraints.

8.2 SUMMARY OF PROJECT FINDINGS

8.2.1 Source Control (Task 2)

NDMA is commonly detected in untreated wastewater. At some wastewater treatment plants, average influent NDMA concentrations are roughly equivalent to effluent concentrations, exceeding the California notification level (10 ng/L) by approximately an order of magnitude. Utilities are therefore interested in assessing the potential benefits of source control.

NDMA was detected in wastewater influent or primary effluent at each of the seven different wastewater treatment plants sampled during this study. Concentrations ranged from 10 to 400 ng/L of NDMA, with a median concentration of 83 ng/L. There was a distinct trend of increasing NDMA concentrations in industrial areas compared with those in residential areas. Industrial discharges to the treatment plants sampled in this study ranged from less than 2% to 18% by volume of total plant flow.

NDMA precursors ranged from 1680 ng/L to 17,900 ng/L, with a median concentration of 4570 ng/L in wastewater influent. NDMA precursors were also higher in industrial areas. The known precursor DMA ranged from 43 to 120 µg/L with a median concentration of 78 µg/L in wastewater influent. DMA did not increase substantially as a result of industrial activities (domestic sewage contains DMA), indicating that other organic nitrogen precursors are contributing to the increase in NDMA precursors observed in industrial areas.

To confirm NDMA discharges from specific industrial processes, samples were collected from two metal plating industries in the OCSD collection area: one which used DTC for metal chelation during waste pretreatment and one that used a non-DTC process. NDMA concentrations were nearly 150 times greater in the wastewater from the DTC process (4230 ng/L compared with 29 ng/L). NDMA precursors were 20 times greater in the DTC process waste. Alternatives to DTC are commercially available for metal treatment; however, the alternatives may not be as effective in pretreating industrial wastewater.

NDMA can also form in residential areas from applying DTC-based herbicides directly to sewer trunklines to control tree root growth. Samples were collected from OCSD trunklines in a residential area before and during application of a DTC-based fumigant marketed for root control. A grab sample collected during herbicide application contained 2400 ng/L of NDMA and 89,000 ng/L of total NDMA precursors. Prior to herbicide application, a 12-h composite sample collected at the same location detected only 40 ng/L of NDMA and 8150 ng/L of NDMA precursors. Root control activities may elevate NDMA concentrations entering the treatment plant by 50 to 100 ng/L over a 1- to 2-h period. The prevalence of herbicide usage in sewer trunklines is unknown; a query of CalPIP returned no results for application of metam sodium products to sewers, suggesting that applications are not regularly reported.

8.2.2 Fate of NDMA and NDMA Precursors during Conventional Treatment (Task 3)

Primary treatment removed a negligible amount of NDMA, as expected, since NDMA is highly soluble and has a low affinity for particles. During activated sludge treatment, NDMA removal was variable: at some facilities, removal rates ranged from 50% to 90%; at others, it ranged from 0% to 25%. At two facilities where sampling efforts were concentrated, NDMA removal varied from day to day, ranging from little or no removal to 90%. There were no obvious explanations for this day-to-day variability, such as treatment plant upsets or variations in influent water quality.

NDMA precursors were well-removed (60%–90% removal) during activated sludge treatment, resulting in secondary effluent concentrations of NDMA precursors ranging from 660 to 2800 ng/L. Exceptions noted at two facilities were explained by the use of wastewater treatment plant polymers that acted as NDMA precursors. The known NDMA precursor DMA was well-removed (96% to 99%) during activated sludge treatment. Since the majority of DMA is removed by secondary treatment, less than 5% of NDMA precursors remaining in secondary effluent are attributable to DMA. Future research should focus on identifying and removing the remaining organic nitrogen precursors.

Significant levels of NDMA may form when secondary effluent containing ammonia is subjected to chlorine disinfection. NDMA increased from 20 to 540 ng/L (median increase of 120 ng/L) during chlorination at LACSD's Whittier Narrows facility in the presence of 1 mg/L of ammonia. Final effluent concentrations of NDMA ranged from 50 to 640 ng/L (the median final chlorinated effluent concentration was 164 ng/L). In contrast, little NDMA formation was observed during chlorine disinfection in nitrified effluent where the ammonia concentration was less than 0.1 mg/L. These results are consistent with laboratory studies indicating that disinfection with free chlorine (i.e., HOCl) results in much less NDMA than disinfection with chlorine in the presence of ammonia (i.e., chloramines).

8.2.3 Fate of NDMA and NDMA Precursors during Advanced Treatment (Task 4)

The commonly employed treatment train MF-RO-UV is fairly effective in reducing NDMA concentrations below the California notification level (10 ng/L). Future research should focus on improving process reliability and cost effectiveness of this treatment train. NDMA concentrations increased during microfiltration due to addition of chlorine prior to the microfilters to control biological growth and membrane fouling. Reverse osmosis removed approximately 50% of the NDMA. Despite the relatively poor performance of MF-RO for removing NDMA, the MF-RO system successfully removed all the remaining NDMA precursors (greater than 98% removal through the RO system). NDMA precursor concentrations in RO effluent were similar to actual NDMA concentrations.

UV systems are capable of treating NDMA levels to below the 10-ng/L California notification level, as illustrated by UV effluent concentrations at OCWD and West Basin (Chapter 5). Implementing MF-RO prior to UV eliminates the concern of NDMA formation from remaining precursors downstream of UV treatment if the wastewater is subjected to chloramination. UV treatment can be costly, since UV doses required for NDMA destruction (1000 mJ/cm^2) are approximately an order of magnitude higher than those used for virus removal (Liang, 2002; MOEE, 1994). Models have been developed to help utilities predict treatment costs and performance as a function of influent water quality.

8.2.4 Modeling NDMA Destruction Using UV Treatment (Task 5)

UV treatment is currently the most effective and widely used method of removing NDMA from treated wastewater. However, treatment costs can vary dramatically due to influent water quality and reactor configuration, from less than $0.08/kgal to $4.00/kgal ($25/acre-ft to $1300/acre-ft) (Chapter 6). Utilities may be able to reduce their treatment costs by altering the UV dose, pretreatment steps, or by blending UV effluent prior to reinjection.

To predict how changes in the treatment train would affect UV treatment system performance and cost, modeling was performed by McGuire Environmental Consultants as Task 5. The most significant fraction of O&M costs for UV treatment systems is electricity consumption, which can be theoretically predicted as a function of influent water quality, reactor configuration, and lamp type. Using several mathematical relationships described in Chapter 6, the project team modeled NDMA removal and the associated cost as a function of influent water quality. Since full-scale UV treatment systems at OCWD and the West Basin Municipal Water District were still under construction at the time, modeling predictions were compared with results from pilot-scale data. These pilot studies were conducted at the West Basin Municipal Water District using four different UV treatment systems, Wedeco LPHO, Atlantic LPHO, Severn Trent MP, and Trojan LPHO, as part of vendor qualification for the full-scale system.

The model was used to calculate theoretical NDMA removal and UV treatment costs. As demonstrated by pilot study results, nonideal reactor hydraulics can lead to less than ideal performance. Changes in flow rate through the UV reactor (which is fixed in diameter and pressurized) affect the velocity and average residence time for each water parcel. This affects NDMA removal rates, making NDMA removal a function of flow rate. Despite this nonideal behavior, pilot study results agreed fairly well with model predictions of the EE/O (Chapter 6, Fig. 6-9 through 6-12). The actual measured EE/O values were on average 13% higher than predicted EE/Os (median, 14%; range observed from –73% to 142% of predicted EE/Os). Modeled NDMA effluent concentrations for the pilot-scale Trojan unit, for example, were underpredicted by an average of 45% (median, 16% underpredicted; ranging from 191% underpredicted to 3% overpredicted). Electricity costs would be underpredicted by an average of 22% (range from 54% underpredicted to 8% overpredicted). The model could be improved by adding an empirically derived baffling factor or an effective path length to account for nonideal reactor hydraulics.

The effect of advanced oxidation on NDMA was also modeled. Advanced oxidation using UV and H_2O_2 may be needed to treat emerging contaminants, such as 1,4-dioxane, and unidentified organic compounds. The model used a steady-state hydroxyl radical approximation. Although hydroxyl radicals compete with NDMA for UV light, recent research has shown that relatively high (50 to 100 mg/L) concentrations of peroxide are necessary to produce this competitive effect (Sharpless and Linden, 2003). The model demonstrated that low peroxide concentrations on the order of 1 to 5 mg/L would not hinder NDMA removal and that the application of 5 mg/L of peroxide during UV treatment would result in 15–80% removal of a typical unidentified organic compound reacting at diffusion-controlled rates with hydroxyl radicals.

8.2.5 Nonpotable Reuse (Project Addendum)

To meet California Title 22 regulatory requirements and to prevent biological growth in the reclaimed water distribution system, wastewater effluent that is used for agriculture and landscaping is usually disinfected with higher chloramine doses than effluent that is recharged or discharged to surface waters. It is therefore possible that much higher concentrations of NDMA form in nonpotable water reuse systems.

Results from sampling of several full-scale nonpotable water reuse systems indicate that NDMA is present in the irrigation water at concentrations ranging from less than 10 ng/L to approximately 600 ng/L. The form of chlorine applied during disinfection (i.e., the presence or absence of ammonia in the treated wastewater during chlorine addition) was the most important variable affecting the concentration of NDMA in the nonpotable water systems. The median concentration of NDMA formed during disinfection in systems using chloramines was 340 ng/L, compared to a median of less than 10 ng/L in systems where free chlorine acted as the disinfectant. This is a significant increase, considering that the median concentration of NDMA in wastewater effluent prior to disinfection was 46 ng/L with a maximum concentration of 380 ng/L (Chapter 3).

In systems using chloramines as disinfectant, a relationship was observed between the concentration of NDMA formed in the disinfection system and the concentration of total NDMA precursors. On the basis of this relationship, it appears that 10–20% of the total NDMA precursors were converted to NDMA in the chlorine disinfection systems studied. This is higher than results measured under conventional municipal wastewater disinfection conditions. For example, at Los Angeles County Sanitation District's Whittier Narrows treatment facility, approximately 5% of the NDMA precursors were converted into NDMA during disinfection (Chapter 3) (Sedlak et al., 2005).

Laboratory experiments were performed using wastewater from several different nonpotable reuse systems. Results confirmed a relationship between chlorine dose and NDMA formation. For the two systems in which significant levels of NDMA formed upon chloramination, a linear relationship was observed between chloramine dose and NDMA formation, although the rate of formation (slope) was different with different systems, probably due to the variation in concentrations of NDMA precursors.

8.3 TECHNICAL CONSIDERATIONS FOR UTILITIES

8.3.1 Characterizing the Problem

Using the information presented in this report and other published literature, utilities can begin to predict NDMA concentrations throughout their facilities and identify areas where they should collect samples or focus on NDMA control strategies, if necessary. For example, if a utility receives more than 10% industrial discharges, average influent NDMA concentrations are likely to range between 100 and 400 ng/L. Removal during secondary treatment is highly variable and may require several days of sampling to determine whether it is significant. Advanced treatment using thin-film composite membrane RO is likely to remove approximately 50% of the NDMA and to completely remove NDMA precursors.

With this general sense of NDMA concentrations throughout the plant, a preliminary sampling plan can be prepared, if necessary. For example, a utility may wish to sample before and after chlorine addition to better estimate the amount of NDMA forming within the treatment plant during chloramination. Sample collection and analytical considerations are discussed in the following section.

In this project, 24-h composite samples were collected to minimize the effect of temporal wastewater variation associated with grab samples. As illustrated by a series of grab samples collected from the influent at OCSD's Plant 1, NDMA concentrations can vary by several orders of magnitude throughout the day, presumably due to batch discharges from industrial processes. Even at wastewater treatment plants located in nonindustrial facilities, the complex matrix of wastewater may result in variation in NDMA concentrations from one grab sample to the next. Collecting composite samples will allow results from several wastewater treatment facilities to be meaningfully compared. Since diurnal variations are averaged by the 24-h composite sample, start and end times of sample collection do not need to be standardized among different wastewater treatment facilities. Refrigerated composite autosamplers are commonly available at wastewater treatment plants.

The NDMA precursor test used in this project provided a meaningful quantification of total organic precursors available for reaction with chloramines to form NDMA. The test was developed at the University of California at Berkeley, as detailed in a recent publication (Mitch et al., 2003a). The test consists of adding pH buffer and a large dose of monochloramine (140 mg/L as Cl_2) to the water sample and allowing monochloramines and organic precursors to react completely over 5 to 10 days, forming NDMA and a variety of other products. The sample is then diluted and analyzed for NDMA. By analyzing samples for total NDMA precursors, utilities are able to distinguish whether or not NDMA precursors are being added within the treatment plant from sources such as wastewater treatment polymers and whether or not NDMA precursors are being removed or destroyed by treatment processes.

NDMA analytical methods have still not been formally approved by the U.S. EPA. Analytical methods with low detection limits (i.e., GC/MS/MS) are not commercially available at most laboratories. The lack of widely available analytical methods is currently the limiting factor for regulating nitrosamines such as NDMA at low (nanograms per liter) levels. This research need is being addressed by an ongoing project sponsored by the WateReuse Foundation titled “Development of low cost analytical methods for measuring NDMA concentrations” (WRF-01-001). Utilities with the analytical capability to detect these contaminants at low levels are at the forefront of NDMA research and will be better prepared to address NDMA when future regulations are established, such as the California Final Recharge and Reuse Requirements.

Utilities that do not have the analytical capability to run NDMA analyses may wish to consider partnering with a research laboratory or another utility with analytical capabilities. Working with research partnerships sponsored by organizations such as the WateReuse Foundation can provide utilities with opportunities to leverage their available resources and adopt suitable strategies for minimizing NDMA.

8.3.2 Source Control

NDMA and NDMA precursor concentrations are well-correlated with industrial activity in the wastewater treatment collection area (Chapter 3). These findings suggest that some utilities may benefit from source control methods, such as pretreatment programs and discharge permit restrictions for selected industries. Restricting individual dischargers of NDMA and NDMA precursors would be effective in reducing treatment plant effluent concentrations if NDMA is not well-removed during conventional treatment.

However, source control is not a viable substitution for advanced treatment; NDMA and NDMA precursor concentrations from domestic sewage are still high enough to form NDMA in excess of the California notification level after activated sludge treatment, filtration, and chlorine disinfection. Source control activities may reduce pulses of NDMA entering the treatment plant from industrial batch discharges, stabilizing any diurnal variations in NDMA concentrations in the UV treatment system influent. This may improve effluent quality, since UV systems are often designed to achieve a fixed removal efficiency (i.e., increases in influent concentrations would result in higher effluent concentrations).

8.3.3 Maximizing NDMA Removal during Conventional Treatment

As described in Chapter 4, conventional activated sludge treatment did not consistently remove NDMA. Some treatment plants exhibited low removal (0–25%), others demonstrated high removal (50–90%), and others removed variable amounts of NDMA (0–90%). There was no obvious reason for the variability in NDMA removal, such as plant upsets, changes in operating procedures, or variations in influent wastewater quality. Utilities may be able to improve NDMA removal during conventional activated sludge treatment if the removal mechanism is identified through further research.

Avoiding the use of Mannich-type polymers (i.e., polyacrylamide and methyl amine functional groups) may reduce NDMA concentrations. Increases in both NDMA and NDMA precursors have been observed during sampling events at facilities using these wastewater treatment polymers. The increase in NDMA and NDMA precursors at these facilities may have been caused by the practice of recycling filter backwash water containing polymers. If the polymer is needed to improve filtration efficiency, there may be an alternative for managing filter backwash water. The NDMA precursor test will indicate whether or not treatment plant polymers or other NDMA precursors are being added within the plant.

8.3.4 Controlling NDMA Formation during Disinfection

There are several options for reducing NDMA formation during disinfection. It may be possible to minimize in-plant NDMA formation by using an alternative disinfectant (e.g., ClO_2) or by modifying the frequency and dose of disinfectant used to prevent membrane fouling (e.g., shock chlorination). However, these practices may not meet manufacturer specifications for microfilter membrane care. Manufacturer warranties can be voided if alternative disinfectant practices are used. Additional research, possibly in cooperation with membrane manufacturers, would be useful as a means of identifying appropriate alternative disinfection methods.

Conditions that reduce NDMA formation include denitrifying wastewater to remove ammonia prior to chlorine addition, preforming monochloramines to prevent the formation of dichloramine, and maintaining an elevated or reduced pH value during chlorination. Since chlorination has been shown to form less NDMA than chloramination, utilities struggling with NDMA control options should consider whether or not they can convert to free chlorine applied in the absence of ammonia. Wastewater utilities that practice nitrification-denitrification produce less NDMA during chlorine disinfection. The use of free chlorine as a disinfectant can slow NDMA formation by approximately an order of magnitude (Mitch and Sedlak, 2002a). The difference in NDMA formation in nitrified effluent and nonnitrified effluent is also illustrated in Chapter 7, Figures 7-15 and 7-21.

Utilities may need to practice chloramination in order to comply with discharge standards for other disinfection byproducts, such as total trihalomethanes. For these utilities, another control option is to preform monochloramines prior to adding the disinfectant to the wastewater. As illustrated in Chapter 5, Figure 5-8, monochloramines can be preformed by adding HOCl first and adding ammonia second, so that a low Cl/N ratio is locally present in the mixing zone. In this environment, monochloramines form but dichloramines do not. In contrast, when HOCl is added to wastewater that contains ammonia, a high Cl/N ratio is present in the mixing zone, encouraging the formation of dichloramines. Since dichloramines react to produce more NDMA than monochloramines, NDMA formation can be minimized by preforming monochloramines.

In addition, by increasing pH, NDMA formation during microfiltration can be reduced, as demonstrated by pilot-scale testing at West Basin. It may be practical to lower the pH with carbon dioxide or a mineral acid prior to adding chlorine. Results from the pilot-scale testing at the West Basin Municipal Water District indicated that utilities could decrease NDMA effluent concentrations by 45 ng/L by following these practices (i.e., increasing the pH to 8.0 and preforming monochloramines prior to addition in wastewater).

NDMA formation during chloramination is also directly related to the amount of NDMA precursors present in the treated wastewater. At facilities using MF-RO, NDMA precursors were similar in magnitude to actual NDMA levels, indicating that the precursors had been well-removed during RO treatment. Improving NDMA precursor removal is a way to ensure that NDMA concentrations remain low throughout the treatment train process, especially if the wastewater is chlorinated after UV treatment. To improve the overall system performance, it is better to keep NDMA precursors from reacting with chloramine to form NDMA prior to RO treatment.

8.3.5 Removal by UV Treatment

The theoretical UV photolysis model described in Chapter 6 will benefit utilities that are interested in predicting the impact of influent water quality, reactor configuration, and hydrogen peroxide concentration on NDMA removal by UV technologies. Utilities will be able to use this model to predict how changes in water quality will affect electricity requirements and associated UV treatment costs. In highly treated wastewater (i.e., reverse osmosis permeate), concentrations of species that typically compete for UV light, such as nitrate, nitrite, iron, DOC, and hypochlorite, are low, simplifying the modeling inputs. Regardless of the UV reactor configurations available, pilot testing results from West Basin demonstrate that electrical costs for NDMA removal from highly treated wastewater are similar. Modeling results demonstrate that lower EE/Os and lower costs can be achieved using reactors with longer path lengths. Results suggest that model deviations from observed values will decrease in full-scale systems; the effects of nonideal reactor hydraulics in pilot-scale systems that are not captured in the water quality model may be less pronounced in full-scale systems.

In order to comply with proposed requirements for advanced oxidation, certain utilities practicing water reuse may need to add hydrogen peroxide to UV systems. However, previous research has demonstrated that the addition of hydrogen peroxide does not significantly improve NDMA removal (Sharpless et al., 2001). As demonstrated in Chapter 5, NDMA precursors are completely removed during reverse osmosis treatment, making post-reverse osmosis treatment by advanced oxidation unnecessary. However, using the steady-state approximation of hydroxyl radicals and assuming a diffusion-controlled reaction rate for a generic unknown organic compound, utilities can use simple modeling to predict removal rates of uncharacterized organic compounds at hydraulic residence times that are characteristic of their UV treatment systems. For example, in the pilot studies conducted at West Basin, only 15% removal of uncharacterized organic compounds was predicted at the higher flow rates (1000 gpm) tested, assuming a hydrogen peroxide dose of 5 mg/L. At the lowest flow rates (100 gpm), approximately 80% removal was predicted.

8.3.6 Reducing NDMA Formation in Nonpotable Reuse Systems

Preliminary sampling and laboratory bench-scale study results indicate that NDMA concentrations in nonpotable reuse systems may exceed the California notification level by more than an order of magnitude. Strategies for utilities to reduce NDMA concentrations in nonpotable systems include those suggested for minimizing formation during disinfection in nonpotable systems:

- Implement nitrification to reduce ammonia concentrations prior to chlorination (i.e., practice chlorination instead of chloramination).
- Reduce NDMA precursor concentrations prior to disinfection by using advanced treatment such as reverse osmosis.
- Reduce the dose of chlorine used during disinfection to the maximum extent possible, provided that microbial targets are being met. Use an alternative process for disinfection, such as UV treatment, perhaps in conjunction with chlorine disinfection.
- Reduce NDMA concentrations prior to disinfection by sunlight systems or UV treatment.

When nitrified effluent is used in nonpotable water systems, NDMA concentrations in chlorinated wastewater effluent can be significantly lower than nonnitrified effluent. Concentrations may be less than the California drinking water notification level of 10 ng/L. In the three systems in which nitrified wastewater effluent was used, little if any NDMA formation was observed in the treatment system or during laboratory chlorination studies. In contrast, systems using chloramines formed NDMA concentrations in excess of 400 ng/L over a 24-h period, particularly in the presence of high NDMA precursor concentrations (i.e., greater than 1000 ng/L). Under the chlorination conditions present in the nonpotable reuse systems sampled in this preliminary study, approximately 10–20% of NDMA precursors were converted to NDMA during chlorination.

An alternative approach to minimizing the concentration of NDMA in nonpotable water reuse systems involves a combination of ultraviolet disinfection and a lower concentration of chlorine to serve as a residual disinfectant in the distribution system. Unlike chlorine disinfection systems, UV treatment systems will not result in the production of NDMA. Furthermore, the UV radiation typically employed in nonpotable water reuse systems might result in partial degradation of some of the NDMA. Additional research is needed to evaluate the potential for formation of NDMA by addition of residual chlorine.

Nonpotable recycled water is commonly used for agricultural irrigation or landscaping purposes. If space is readily available, open holding basins may be employed instead of UV treatment to reduce NDMA concentrations using natural sunlight. In early work conducted by OCWD, complete removal of NDMA was observed in less than 3 h in full sunlight conditions, starting with an initial NDMA concentration of 600 ng/L (Soroushian et al., 2001). Based on the results of this test, wastewater was channeled into open holding basins with a theoretical retention time of 1.5 h. This full-scale system resulted in good NDMA removal, ranging from 12% to 65% as measured using grab samples (Soroushian et al., 2001). One drawback of this method is the possibility of microbial fouling in the holding basins or the formation of additional NDMA if the water is rechloraminated.

8.4 FUTURE RESEARCH NEEDS

8.4.1 Investigation of Other Nitrosamine Compounds

NDMA is just one example of a family of potent carcinogenic nitrosamine compounds. Because of the structural similarity to NDMA and similar chemical and physical properties, other nitrosamines may form during wastewater treatment. In September 2004, California established a notification level of 10 ng/L for *N*-nitrosodiethylamine (NDEA). The same action level was established for *N*-nitrosodipropylamine in May 2005 following the detection of *N*-nitrosodipropylamine and NDMA in disposable resins that were being evaluated for drinking water treatment (CalDHS, 2005c). California's draft Title 22 recharge and reuse requirements may specify monitoring for NDEA and *N*-nitrosopyrrolidine (CalDHS, 2003).

Although analytical methods to detect low levels of other nitrosamines have not been developed by many utilities, preliminary research indicates the presence of other nitrosamines in wastewater. For example, *n*-nitrosomorpholine was found in several wastewater treatment plants prior to chlorine addition. *N*-Nitrosopyrrolidine and *N*-nitrosodibutylamine formed at concentrations ranging from 20 to 40 ng/L during wastewater chloramination (Hwang et al., 2004). NDEA concentrations were typically below 5 ng/L but were detected as high as 30 ng/L at another treatment facility. Other nitrosamines were included in the analysis but were not detected: *N*-nitrosoethylmethylamine and *N*-nitrosopiperidine (Hwang et al., 2004).

8.4.2 Fate during Conventional Treatment: Mass Balance Approach

As discussed in Chapter 4, NDMA removal during activated sludge treatment was not consistent. At some facilities, NDMA concentrations decreased during secondary treatment by 50–90%. At other facilities, little or no removal occurred (0–25% removal). Day-to-day variability was observed at several treatment plants where sampling efforts were concentrated. For example, at the SJ/SC WPCP, average daily NDMA removal ranged from 0 to 75% during 1 week of sampling. The reason has not yet been determined. Hypotheses that would need future research to confirm or abandon include the impact of natural sunlight photolysis in secondary treatment tanks that are open to the atmosphere, changes in biological activity or microbial populations, and the impact of water quality or dilution from recycling other flow streams through secondary treatment processes, such as filtration backwash water.

8.4.3 Subsurface Monitoring

Another relevant research topic is the fate and transformation of NDMA as groundwater percolates through the vadose zone, either intentionally in a water recharge project or unintentionally following agriculture or landscape irrigation. Recent research indicates a high tendency of NDMA to leach through the soil, particularly in areas where soil organic content is low and vegetation is sparse (i.e., microbial activity is low) (Yang et al., 2005). Further research on the persistence or microbial degradation of NDMA in the vadose zone may clarify the implications of current nonpotable reuse practices.

REFERENCES

Agency for Toxic Substances and Disease Registry (ATSDR). Toxicological profile of N-nitrosodimethylamine; U.S. Department of Health and Human Services, Public Health Service: Atlanta, 1989.

American Public Health Association (APHA). *Standard Methods for the Examination of Water and Wastewater*, 20th ed. American Public Health Association, American Water Works Association, Water Environment Federation: Washington, D.C., 1998.

Bolton, J. R.; Stefan, M. I. Fundamental photochemical approach to the concepts of fluence (UV dose) and electrical energy efficiency in photochemical degradation reactions; *Res. Chem. Intermediates* **2002,** *28*, 857–870.

Bolton, J. R. Non-disinfection based UV applications. *Conference Proceedings from the First International Congress on Ultraviolet Technologies*, Washington, DC, 2001.

Bolton, J. R. Advanced oxidation UV treatment of organic pollutants in drinking water. *IUVA News* **2002**, *4(3)*, 16–19.

CalDHS. Studies on the occurrence of NDMA in drinking water; last updated March 15, 2002; California Department of Health Services: Sacramento, CA; http://www.dhs.ca.gov/ps/ddwem/chemicals/NDMA/studies.htm, 2002.

CalDHS. Draft groundwater recharge and reuse regulations, Title 22, California Code of Regulations, Division 4; Chapter 3, Environmental Health, Recycling Criteria; July 21 with initial note added December 18; California Department of Health Services: Sacramento, CA; http://www.dhs.ca.gov/ps/ddwem/publications/waterrecycling/rechargeregulationsdraft-12-01-04.pdf, 2003.

CalDHS. NDMA laboratory analyses; last updated March 4, 2005; California Department of Health Services: Sacramento, CA; http://www.dhs.ca.gov/ps/ddwem/chemicals/NDMA/NDMAlabs.htm, 2005a.

CalDHS. DHS drinking water notification levels. California Department of Health Services Drinking Water Program: Sacramento, CA; http://www.dhs.ca.gov/ps/ddwem/chemicals/AL/notificationoverview.pdf, 2005b.

CalDHS. A brief history of NDMA findings in drinking water supplies; last updated Feb. 22, 2005; California Department of Health Services: Sacramento, CA; http://www.dhs.ca.gov/ps/ddwem/chemicals/NDMA/history.htm, 2005c.

Calgon Carbon Corporation. Report of the treatment of NDMA by Calgon Carbon Corporation's UV-based process. Calgon Carbon: Pittsburgh, PA, 2000.

Calgon Carbon Corporation. Report of the on-site testing of the Rayox UV treatment system; prepared for La Puente Valley County Water District; Calgon Carbon: Pittsburgh, PA, 2002; pp. 1–37.

CalPIP. California Pesticide Information Portal; California Department of Pesticide Regulation: Sacramento, CA; http://calpip.cdpr.ca.gov/cfdocs/calpip/prod/main.cfm, 2005.

Carr, S. A.; Neisess, L. B.; Rinaldi, K.; Chandler, W.; Tang, A. The impact of antifreeze waste on effluent NDMA concentrations. County Sanitation Districts of Los Angeles County, San Jose Creek Water Quality Laboratory. Poster presentation at the WateReuse Foundation 2003 Annual Research Conference, South San Francisco, CA, June 2–3, 2003.

CHEMLIST. CHEMLIST database. http://www.cas.org/CASFILES/chemlist.html, 2002.

Child, P.; Kaa, G.; Benitz, D.; Fowlie, P.; Hong-You, R. Reaction between chlorine and a dimethylamine containing polyelectrolyte leading to the formation of N-nitrosodimethylamine. Proceedings of the American Water Works Association 1996 Annual Conference, Water Research, Vol. C, Toronto, Ontario, June 23–27, 1996.

Choi, J.; Valentine, R. L. N-nitrosodimethylamine formation by free-chlorine-enhanced nitrosation of dimethylamine. *Environ. Sci. Technol.* **2003,** *37*, 4871–4876.

Choi, J.; Valentine, R. L. Formation of N-nitrosodimethylamine (NDMA) from reaction of monochloramine: a new disinfection by-product. *Water Res.* **2002,** *36*, 817–824.

Choi, J.; Duirk, S. E.; Valentine, R. L. Mechanistic studies of N-nitrosodimethylamine (NDMA) formation in chlorinated drinking water. *J. Environ. Monitoring* **2002,** *4*, 249–252.

Chow, Y. L. Nitrosamine photochemistry: reactions of aminium radicals. *Accounts Chem. Res.* **1973,** 6, 354–360.

Code of Federal Regulations (CFR). Water quality standards, establishment of numeric criteria for priority toxic pollutants for the State of California, rule, part III; U.S. Environmental Protection Agency; **2000,** 40 *CFR* 131; *Fed. Reg.* 65(97), Thursday May 18.

Crittenden, J. C.; Hu, S.; Hand, D. W.; Green, S. A kinetic model for H_2O_2/UV process in a completely mixed batch reactor. *Water Res.* **1999,** *33*, 2315–2328.

Cushing, R.S.; Mackey, E.D.; et al. Impact of common water treatment chemicals on UV disinfection. American Water Works Association Annual Conference Proceedings, **2001**.

Dietrich, A. M.; Gallagher, D. L.; DeRosa, P. M.; Millington, D. S.; DiGiani, F. A. Enhancement of N-nitrosodimethylamine formation on granular-activated carbon from N-methylaniline and nitrite. *Environ. Sci. Technol.* **1986,** *20*, 1050–1055.

DiGiano, F. A.; Carrier, R. A.; Dietrich, A. M. Nitrification and nitrosation on the surface of GAC. *J. Am. Water Works Assoc.* **1986,** *78*, 70–74.

Fitzsimmons, S. Personal communication regarding Orange County Water District laboratory detection limit for NDMA; 2004.

Fleming, E. C.; Pennington, J. C.; Wachob, B. G.; Howe, R. A.; Hill, D. O. Removal of N-nitrosodimethylamine from waters using physical-chemical techniques. *J. Haz. Mater.* **1996,** *51*, 151–164.

Gerecke, A. C.; Sedlak, D. L. Precursors of N-nitrosodimethylamine in natural waters. *Environ. Sci. Technol.* **2003,** *37*, 1331–1336.

Graham, J. E.; Andrews, S. A.; Farquhar, G. J.; Meresz, O. Thiram as an NDMA precursor in drinking water treatment. Proceedings (Water Research), American Water Works Association Annual Conference, Toronto, Ontario, **1996,** pp. 15-27.

Gui, L.; Gillham, R. W.; Odziemkowski, M. S. Reduction of N-nitrosodimethylamine with granular iron and nickel-enhanced iron. 1. Pathways and kinetics. *Environ. Sci. Technol.* **2000,** 34, 3489–3494.

Hanst, P. L.; Spence, J. W.; Miller, M. Atmospheric chemistry of N-nitrosodimethylamine. *Environ. Sci. Technol.* **1977,** *11,* 403–405.

Hartwell. Hartwell Corp. v. Ventura Superior Court; 27 Cal. 4th 256, 2002.

HSDB (Hazardous Substances Data Bank). National Library of Medicine Specialized Information Services, National Institutes of Health: Bethesda, MD; http://toxnet.nlm.nih.gov/, 2005.

Hwang, C. J.; Guo, Y. C.; Krasner, S. W. Contribution of treated wastewater to nitrosamine occurrence and formation in drinking water. Presented at the 227th American Chemical Society National Meeting, Anaheim, CA, March 28, 2004.

Hwang, Y.; Matsuo, T.; Hanaki, K.; Suzuki, N. Removal of odorous compounds in wastewater by using activated carbon, ozonation and aerated biofilter. *Water Resources* **1994,** *28,* 2309–2319.

Hwang, Y.; Matsuo, T.; Hanaki, K.; Suzuki, N. Identification and quantification of sulfur and nitrogen containing odorous compounds in wastewater. *Water Resources* **1995,** *29*, 711–718.

Kommineni, S.; Ela, W. P.; Arnold, R. G.; Huling, S. G.; Hester, B. J.; Betterton, E. A. NDMA treatment by sequential GAC adsorption and Fenton-driven destruction. *Environ. Eng. Sci.* **2003,** *20*, 361–373.

Lem, W. Application of a medium pressure UV system for the treatment of N-nitrosodimethylamine (NDMA). Calgon Carbon Corporation: Pittsburgh, PA, 2003.

Liang, S. Photolysis and advanced oxidation processes for NDMA removal from drinking water. Presentation at the Fourth Symposium in the Series on Groundwater Contaminants: Perchlorate and NDMA in Groundwater: Occurrence, Analysis and Treatment; Groundwater Resources Association of California, Baldwin Park, CA, April 17, 2002.

Liang, S.; Min, J. H.; Davis, M. K.; Green, J. F.; Remer, D. S. Use of pulsed-UV processes to destroy NDMA. *J. Am. Water Works Assoc.* **2003,** *95*, 121–131.

Loveland, J. N-nitrosodimethylamine (NDMA): current status for drinking water and reclaimed water applications. Presented at the Los Angeles Department of Water and Power Technology Transfer Workshop, July 2002.

MacDonald, A. Perchlorate and NDMA contamination in the Sacramento area. Presentation at the Fourth Symposium in the Series on Groundwater Contaminants: Perchlorate and NDMA in Groundwater: Occurrence, Analysis and Treatment; Groundwater Resources Association of California, Baldwin Park, CA, April 17, 2002.

McGuire Environmental Consultants, Inc. Pilot testing to inhibit N-nitrosodimethylamine (NDMA) formation at the AEP, City of Pomona, 2001.

Mezyk, S. P.; Cooper, W. J.; Madden, K. P.; Bartels, D. M. Free radical destruction of N-nitrosodimethylamine in water. *Environ. Sci. Technol.* **2004,** *38,* 3161–3167.

Mirvish, S. S. Formation of N-nitroso compounds: chemistry, kinetics, and in vivo occurrence. *Toxicol. Appl. Pharmacol.* **1975,** *31*, 325–351.

Mitch, W. A.; Sedlak, D. L. Formation of N-nitrosodimethylamine (NDMA) from dimethylamine during chlorination. *Environ. Sci. Technol.* **2002a,** *36*, 588–595.

Mitch, W. A.; Sedlak, D. L. Prevention of NDMA formation during chlorination. Presentation at the Fourth Symposium in the Series on Groundwater Contaminants: Perchlorate and NDMA in Groundwater: Occurrence, Analysis and Treatment; Groundwater Resources Association of California, Baldwin Park, CA, April 17, 2002b.

Mitch, W. A.; Sedlak, D. L. Characterization and fate of N-nitrosodimethylamine precursors in municipal wastewater treatment plants. *Environ. Sci. Technol.* **2004,** *38*, 1445–1454.

Mitch, W. A.; Gerecke, A. C.; Sedlak, D. L. An N-nitrosodimethylamine (NDMA) precursor analysis for chlorination of water and wastewater. *Water Res.* **2003a,** *37*, 3733–3741.

Mitch, W. A.; Oelker, G. L.; Hawley, E. L.; Deeb, R. A.; Sedlak, D. L. Minimization of NDMA formation during chlorine disinfection of municipal wastewater by application of pre-formed chloramines. *Environ. Eng. Sci.* **2005,** *22*, 882–890.

Mitch, W. A.; Sharp, J. O.; Trussell, R. R.; Valentine, R. L.; Alvarez-Cohen, L.; Sedlak, D. L. N-nitrosodimethylamine (NDMA) as a drinking water contaminant: a review. *Environ. Eng. Sci.* **2003b,** *20*, 389–404.

MOE. Drinking water surveillance program summary report for 2000, 2001 and 2002. Ontario Ministry of the Environment: Ontario; http://www.ene.gov.on.ca/envision/water/dwsp/0002/index.htm, 2004.

MOEE. Removal of N-nitrosodimethylamine from the Ohsweken (Six Nations) water supply, final report. Ontario Ministry of Environment and Energy: Ontario, 1994.

Mofidi, A. A.; Coffey, B. M.; et al. Using ultraviolet light to achieve multiple water quality objectives. American Water Works Association Water Quality Technology Conference Proceedings; American Water Works Association: Washington, DC, 2000.

Montgomery, James M. Operation, maintenance and performance evaluation of the Potomac Estuary Experimental Water Treatment Plant; NTIS publication, September 1983.

Montgomery Watson Harza (MWH). Water Treatment Principles and Design, 2nd ed. John Wiley & Sons, Inc.: New York, 2005.

Najm, I.; Teefy, S.; Barrett, S. E. NDMA formation from water treatment polymers. American Water Works Association 2004 Annual Conference and Exposition, Orlando, FL, June 13–17, 2004.

Najm, I.; Trussell, R. R. NDMA formation in water and wastewater. *J. Am. Water Works Assoc.* **2001,** *93*, 92–99.

National Research Council (NRC). Issues in potable reuse. *The viability of augmenting drinking water supplies with reclaimed water.* Dobbs, D. A., Ed.; National Academy Press: Washington, DC, 1998.

National Research Council (NRC). *Drinking water and health;* National Academy Press: Washington, DC, 1977.

National Toxicology Program (NTP). N-nitrosodimethylamine, CAS no. 62-75-9; *Eleventh Report on Carcinogens*; National Toxicology Program, Department of Health and Human Services: Washington, DC, 2005.

Nazaroff, William W.; Alvarez-Cohen, Lisa. *Environmental Engineering Science;* Wiley: New York, 2000.

Neisess, L. B.; Baird, R. B.; Carr, S. A.; Gute, J. Can *N*-nitrosodimethylamine formation be affected by polymer use during advanced wastewater treatment? Proceedings of the WateReuse Association's Research Symposium XVIII, San Antonio, TX, September 2003.

NIH NLM. Household products database. National Institute of Health, National Library of Medicine Specialized Information Services: Bethesda, MD; http://householdproducts.nlm.nih.gov, 2004.

Orange County Sanitation District (OCSD). NDMA source control, sources of N-nitrosodimethylamine in the Orange County Sanitation District Service Area, August 2000–November 2001; Source Control Division, Orange County Sanitation District, CA; www.ocsd.com/about/reports/archive.asp, 2002.

Parkhurst, J. D. A plan for water reuse. Report to the Directors of the County Sanitation Districts of Los Angeles County, CA, July 1963.

Pesticide Action Network. PAN pesticides database; http://pesticideinfo.org, 2005.

Recycled Water Task Force. Recycled water task force final report: water recycling, 2003; recommendations of California's Recycled Water Task Force; http://www.owue.water.ca.gov/recycle/taskforce/taskforce.cfm, 2003.

Reinhard, M.; Goodman, N.; McCarty, P.; and Argo, D. Removing trace organics by reverse osmosis using cellulose acetate and polyamide membranes. Journal of the American Water Works Association **1986,** April, 163–174.

Rosenbaum, D. B. Suit cites groundwater risk from disinfection byproduct. *Eng. News Rec.* **2001,** Dec. 24.

Sakamoto, G. UV disinfection of reclaimed wastewater: the North American experience. *Environ. Prot.* **2000,** *11*.

Schreiber, M. I.; Mitch, W. A. The influence of the order of reagent addition on NDMA formation during chloramination. *Environ. Sci. Technol.* **2005,** *39*, 3811–3818.

Schwarzenbach, R. P.; Gschwend, P. M.; Imboden, D. M. *Environmental Organic Chemistry;* John Wiley and Sons, Inc.: New York, 1993.

Sedlak, D. L.; Deeb, R. A.; Hawley, E. L.; Mitch, W. A.; Durbin, T. D.; Mowbray, S.; Carr, S. Sources and fate of nitrosodimethylamine and its precursors in municipal wastewater treatment plants. *Water Environ. Res.* **2005,** *77*, 32–39.

Shapley D. Nitrosamines: scientists on the trail of prime suspect in urban cancer. *Science* **1976,** *191*, 268–270.

Sharp, J. O.; Alvarez-Cohen, L. Biodegradation of N-nitrosodimethylamine by monooxygenase containing bacteria. *Abstracts of the 102nd General Meeting of the American Society for Microbiology*; ASM Press: Washington, DC; 2002.

Sharpless, C. M.; Linden, K. G. Experimental and model comparisons of low- and medium-pressure Hg lamps for the direct and H_2O_2 assisted UV photodegradation of N-nitrosodimethylamine in simulated drinking water. *Environ. Sci. Technol.* **2003,** *37,* 1933–1940.

Sharpless, C. M.; Chou, C. I.; Modifi, A. A.; Linden, K. G. N-nitrosodimethylamine removal from drinking water by UV treatment: a direct comparison of different UV technologies. American Water Works Association Water Quality Technology Conference Proceedings; American Water Works Association: Washington, DC, 2001.

Shaw Environmental, Inc. Draft final bench-scale testing summary report for Fenton's reagent bench-scale test, Stringfellow site, Glen Avon, California; 2004.

Smith, P. W. Enhanced oxidation destroys dimethylnitrosamine. *Water Environ. Technol.* **1992,** pp. 67–69.

Smith, R. E. H.; Furgal, J. A.; Charlton, M. N.; Greenberg, B. M.; Hiriart, V.; Marwood, C. Attenuation of ultraviolet radiation in a large lake with low dissolved organic matter concentrations. *Can. J. Fisheries Aquatic Sci.* **1999,** *56*, 1351–1361.

Soroushian, F.; Shen, Y.; Patel, M.; Wehner, M. Evaluation and pilot testing of advanced treatment processes for NDMA removal and reformation prevention. American Water Works Association 2001 Annual Conference Proceedings; American Water Works Association: Washington, DC, 2001.

Spath, David. Memorandum regarding Policy Memo 97-005 Policy Guidance for Direct Domestic Use of Extremely Impaired Sources. Division of Drinking Water and Environmental Management. State of California Department of Health Services. November 5, 1997.

Stefan, M. I.; Hoy, A. R.; Bolton, J. R. Kinetics and mechanism of the degradation and mineralization of acetone in dilute aqueous solution sensitized by the UV photolysis of hydrogen peroxide. *Environ. Sci. Technol.* **1996,** *30,* 2381–2390.

Stumm, W.; Morgan, J. J. *Aquatic Chemistry: An Introduction Emphasizing Chemical Equilibria in Natural Waters*; John Wiley and Sons: New York, 1981.

Swayne, M. D.; Boone, G. H.; Bauer, D.; Lee, J. S. Wastewater in receiving waters at water supply abstraction points. U.S. Environmental Protection Agency: Washington, DC, 1980.

Tricker, A. R.; Pfundstein, B.; Preussmann, R. Nitrosatable secondary amines: exogenous and endogenous exposure and nitrosation *in vivo*. In R. N. Leoppky and C. J. Michejda, Eds., *Nitrosamines and Related N-Nitroso Compounds: Chemistry and Biochemistry*, American Chemical Society: Washington, DC, 1994, pp. 93–101.

Trojan Technologies, Inc. NDMA demonstration testing of Trojan Technologies' low-energy UV treatment system at the perchlorate treatment plant La Puente Valley County Water District; 2001, pp. 1-25.

U.S. Environmental Protection Agency. N-nitrosodimethylamine (CASRN 62-75-9); Integrated Risk Information System (IRIS); U.S. Environmental Protection Agency: Washington, DC; http://www.epa.gov/iris/subst/0045.htm; last significant revision, January 1991.

U.S. Environmental Protection Agency. Record of decision, Aerojet General Corp., EPA ID CAD980358832, OU 03, Rancho Cordova, CA; July 20, 2001.

U.S. Environmental Protection Agency. The HPV voluntary challenge chemical list; http://www.epa.gov/opptintr/chemrtk/hpvchmlt.htm, 2002.

Valentine, R. L.; Brandt, K. I.; Jafvert, C. T. A spectrophotometric study of the formation of an unidentified monochloramine decomposition product. *Water Resources* **1986,** *20,* 1067–1074.

WateReuse Foundation. Investigation of NDMA fate and transport; project WRF-02-002; 2002.

Wentz, S. Personal communication regarding sales of DTC products for industrial wastewater treatment processes; 2004.

West Basin Municipal Water District. N-nitrosodimethylamine studies in recycled water. Presented at the NDMA Workshop on the Removal and/or Destruction of NDMA and NDMA Precursors in Wastewater Treatment Processes: State of the Art Assessment of Sources, Fate and Control. Sponsored by the WateReuse Association, Carson, CA, March 14, 2002.

Whitley Burchett & Associates. NDMA technical memorandum; 2000.

Wilczak, A.; Assadi-Rad, A.; Lai, H. H.; Hoover, L. L.; Smith, J. F.; Berger, R.; Rodigari, F.; Beland, J. W.; Lazzelle, L. J.; Kincannon, E. G.; Baker, H.; Heaney, C. T. Formation of NDMA in chlorinated water coagulated with DADMAC cationic polymer. *J. Am. Water Works Assoc.* **2003,** *95,* 94–106.

Wolfe, R. L.; Olson, B. H. Chloramine disinfection: the implications of interference by nitrogenous organic compounds. *Waterworld News* **1986,** *2,* 12–15.

World Health Organization (WHO). Managing water in the home: accelerated health gains from improved water supply; report no. WHO/SDE/WSH/02.07; Water Sanitation and Health, Department of Protection of the Human Environment; WHO; http://www.who.int/water_sanitation_health/dwq/WSH02.07.pdf, 2002.

Yang, W. C.; Gan, J.; Liu, W. P.; Green, R. Degradation of N-nitrosodimethylamine (NDMA) in landscape soils. *J. Environ. Qual.* **2005,** *34,* 336–341.

Zeisel, S. H.; DaCosta, K. A.; Fox, J. G. Endogenous formation of dimethylamine. *Biochem. J.* **1985,** *232,* 403–408.

APPENDIX A

PROJECT OUTREACH

A.1 SUMMARY OF PROJECT OUTREACH

The WateReuse Foundation and research team both recognized that project findings would be more beneficial to utilities if results were shared with others. By communicating preliminary findings throughout the three-year research time frame, the project would also benefit from the ideas and experiences contributed by others. Throughout the project, the team presented project findings at professional organizations and events, as well as in journal publications. A list of these presentations and publications follows.

Carr, S. A.; Neisess, L. B.; Rinaldi, K.; Chandler, W.; Tang, A. The impact of antifreeze waste on effluent NDMA concentrations. County Sanitation Districts of Los Angeles County, San Jose Creek Water Quality Laboratory. Poster presentation at the WateReuse Foundation 2003 Annual Research Conference, South San Francisco, CA, June 2–3, 2003.

Deeb, R.; Sedlak, D. L.; Hawley, E.; Kavanaugh, M. Sources and fate of NDMA and precursors in wastewater treatment plants. Presented at the Water Environment Federation 77th Annual Technical Exhibition and Conference (WEFTEC), New Orleans, LA, Oct. 4, 2004.

Deeb, R. A. NDMA formation and fate during wastewater treatment: current and future challenges of water reuse. Presented at the Water Environment Federation 76th Annual Technical Exhibition and Conference (WEFTEC), Los Angeles, CA, Oct. 13, 2003.

Deeb, R. A.; Hawley, E. L.; Chowdhury, Z.; Kavanaugh, M. C. NDMA sources, formation and destruction during wastewater treatment: current and future research. Presented at the WateReuse Foundation 2003 Annual Research Conference, South San Francisco, CA, June 2–3, 2003.

Deeb, R. A.; Hawley, E. L.; Laugier, M.; Kavanaugh, M. Emerging chemical contaminants: technical and institutional challenges. Presented at the 13th Annual Groundwater Resources Association Meeting and Conference, Rohnert Park, CA, Sept. 24, 2004.

Deeb, R. A.; Hawley, E. L.; Sedlak, D.; Kavanaugh, M. Emerging concerns over NDMA in groundwater: an overview of NDMA sources, formation, transport and treatment. Presented at the U.S. EPA Technical Support Project Meeting, Sacramento, CA, Oct. 19, 2004.

Deeb, R. A.; Hawley, E. L.; Sedlak, D. L.; Kavanaugh, M. NDMA formation and fate during wastewater treatment: current and future challenges of water reuse. Symposium paper presented before the Division of Environmental Chemistry, American Chemical Society, Anaheim, CA, March 28–April 1, 2004.

Deeb, R. A.; Hawley, E. L.; Sedlak, D. L.; Mitch, B.; Kavanaugh, M. NDMA formation and fate during wastewater treatment: current and future challenges of water reuse. Presented at the American Water Works Association Annual Conference and Exhibition, San Francisco, CA, June 12–16, 2005.

Hawley, E. L.; Deeb, R. A.; Chowdhury, Z.; Kavanaugh, M. NDMA: the challenge “de jour” of water reuse efforts, formation and control during wastewater treatment. Poster presentation at the Malcolm Pirnie, Inc. Technical Symposium, Stamford, CT, April 4–5, 2003.

Hawley, E. L.; Deeb, R. A.; Chowdhury, Z.; Kavanaugh, M. NDMA in recycled water: water supply vs. water quality. Presented at the Malcolm Pirnie, Inc. Technical Symposium, Stamford, CT, April 8, 2005.

Hawley, E. L.; Deeb, R. A.; Sedlak, D. L.; Kavanaugh, M. C. Strategies for controlling NDMA in wastewater facilities. Poster presentation at the WateReuse Foundation 2005 Annual Research Conference, Las Vegas, NV, May 16, 2005.

Hawley, E. L.; Laugier, M.;, Deeb, R. A.; Kavanaugh, M. C. Emerging chemical contaminants: technical, legal and policy challenges. Poster presentation at the WateReuse Foundation 2003 Annual Research Conference, South San Francisco, CA, June 2–3, 2003.

Kavanaugh, M. C. NDMA occurrence, formation and destruction during wastewater treatment: current and future research. Presented at the WateReuse Foundation 2002 Annual Research Conference, Manhattan Beach, CA, June 3–4, 2002.

Loveland, J. P.; Means, E. G. Development of a water quality based model for UV treatment of NDMA and other trace organics in reclaimed water. Poster presentation at the WateReuse Foundation 2003 Annual Research Conference, South San Francisco, CA, June 2–3, 2003.

Mitch, W. A.; Oelker, G. L.; Hawley, E. L.; Deeb, R. A.; Deeb, R. A.; Sedlak, D. L. Minimization of NDMA formation during chlorine disinfection of municipal wastewater by application of pre-formed chloramines. *Environ. Eng. Sci.*, **2005,** *22,* 882–890.

Pehlivanoglu-Mantas, E.; Hawley, E.; Deeb, R. A.; Sedlak, D. L. Formation of nitrosodimethylamine (NDMA) during chlorine disinfection of wastewater effluents prior to use in irrigation systems. *Water Res.*, submitted for publication, 2005.

Sedlak, D. L.; Deeb, R.; Hawley, E.; Mitch, W. A.; Mowbray, S.; Carr, S. Fate of NDMA and precursors during conventional wastewater treatment—implications for source control. Proceedings of the Water Environment Federation 77th Annual Technical Exhibition and Conference (WEFTEC), New Orleans, LA, Oct. 4, 2004.

Sedlak, D. L.; Mitch, W. Factors controlling the formation of N-nitrosodimethylamine (NDMA) during chlorination. Presented at the WateReuse Foundation 2001 Annual Research Conference, Monterey, CA, June 4–5, 2001.

Sedlak, D. L. NDMA: the next disinfection byproduct to worry about? Presented to the University of New South Wales, 2004.

Sedlak, D. L.; Deeb, R. A.; Hawley, E. L.; Mitch, W. A.; Durbin, T. D.; Mowbray, S.; Carr, S. Sources and fate of N-nitrosodimethylamine and its precursors in municipal wastewater treatment plants. *Water Environ. Res.* **2005**, *77,* 32–39.

Sedlak, D. L.; Mitch, W. A.; Gerecke, A. N-nitrosodimethylamine (NDMA): the unexpected disinfection byproduct. Gordon Research Conference, Environmental Sciences: Water. Plymouth, NH, June 2002.

APPENDIX B

SAMPLING AND ANALYTICAL METHODS

B.1 OVERVIEW

Since NDMA monitoring and low-level analytical methods for NDMA in wastewater matrices have only recently become topics of interest, the development of sampling and analytical guidelines for the project was a critical component of the research plan. There is currently no certified analytical method for NDMA or NDMA precursors in drinking water or wastewater matrices. CalDHS has developed guidelines for acceptable analytical approaches and is aware of only six commercial laboratories that are equipped to perform low-level NDMA analyses within these guidelines (CalDHS, 2005a). Similarly, there is little published guidance pertaining to NDMA sample collection. Sampling and analytical guidelines were developed following the March 2002 workshop and incorporated lessons learned and shared at the workshop by project researchers.

B.2 SAMPLING PROTOCOLS

Differences in sample collection methods can result in NDMA measurements spanning one or more orders of magnitude, as seen in historical monitoring data presented during the project workshop. Factors that can contribute to this variation include the type of sample (grab sample vs. composite sample of several grabs), formation or degradation of NDMA in the sample container following sample collection, and matrix effects causing interference during NDMA analysis, particularly in raw sewage. Differences in sample collection method, storage conditions, and holding time prior to extraction also contribute to the variation in results. To avoid problems related to sampling, the project team adopted the following project guidelines and QA/QC techniques.

B.2.1 Use of Composite Samples

Both composite samples and grab samples have benefits and drawbacks. Grab samples capture diurnal variations in NDMA concentrations, perhaps in response to changes in influent water quality or to changes in treatment plant operating conditions. However, grab samples are not representative of the average NDMA concentrations; there is often a large variability in NDMA concentrations in grab samples collected throughout the day. Grab samples collected from two different locations in the treatment plant are hard to stagger precisely (since hydraulic residence time between the two locations is not always known), making it difficult to capture a plug-flow parcel of water as it moves through the treatment plant. For these reasons, it is harder to identify trends in water quality using grab samples unless multiple grab samples are taken over a short period of time.

Composite samples provide a more representative estimate of average NDMA concentrations over a desired period of time. Since NDMA averages are less susceptible to the fluctuations in influent water quality and treatment plant operating conditions, composite sample results are easily compared to each other meaningfully. Therefore, 24-h composite samples were the primary form of samples collected for this project. A series of several grab samples was necessary in some locations (distribution system, trunklines in the collection system) due to logistics of setting up a composite sampler in these locations.

Refrigerated autosamplers were used for sample collection. This was simple to arrange, since most wastewater treatment facilities are already equipped with these autosamplers. Teflon tubing was used to minimize the potential for NDMA precursors from the tubing to contaminate the samples. Autosamplers that are regularly used should not have this problem. Automatic compositing was used to reduce the risk of sample contamination. Equal sample volumes were collected at regular time intervals throughout the sample collection period (e.g., once per hour over a 24-h period).

B.2.2 Container and Preservation Requirements

NDMA samples were collected in amber glass bottles to prevent the compound from photo-degrading by visible light. I-Chem 300 Series-certified (345-2360) 2-L amber glass bottles with Teflon-lined polyethylene screw caps were used. For grab samples collected downstream of chlorine disinfection, sample bottles contained a chlorine quenching agent to react with chloramines and prevent NDMA from continuing to form inside the sample container following sample collection. Chlorine quenching agents used during this project included ascorbic acid (vitamin C), sodium thiosulfate, and sodium sulfite. However, since the addition of ascorbic acid can affect DOC measurements, the latter two chlorine quenching agents were primarily used during the project. Excess chlorine quenching agent (~50 mg/L) was added to each sample bottle, enough to quench up to 8 mg/L of residual Cl_2.

When composite samples were collected, the chlorine quenching agent was added directly to the composite sample container prior to sample collection. The presence of the chlorine quenching agent was previously determined not to affect the results of the NDMA precursor test as long as excess chlorine was added during the test (Fitzsimmons, 2004, personal communication). This enabled the composite sample to be split and analyzed for both NDMA and NDMA precursors when needed.

B.2.3 Field Measurements

Field measurements included free chlorine, total (free and combined) chlorine, water temperature, pH, and other pertinent field observations. Free and total chlorine were measured in a separate sample from that used for NDMA measurements, since the chlorine quenching agent added to the NDMA sample can alter the amount of free chlorine present. When approximate chlorine concentrations were needed to supplement a composite sample of NDMA, chlorine was measured in a grab sample collected at the beginning or end of composite sample collection. The DPD colorimetric method (standard method 4500-Cl G) was used to measure free and combined chlorine.

B.2.4 Sample Labeling, Storage, and Shipping Requirements

Unique sample IDs were assigned to each sample to improve communication between team members and to make it easier to assemble the data into a comprehensive database. Sample ID nomenclature reflects the facility location, location within the treatment plant, sample date, and suffix to indicate duplicate, field blank, etc., when necessary. Since multiple utilities participated in the project, the sample ID may or may not correspond with the nomenclature used by each utility laboratory.

After labeling each sample with a unique sample ID, the samples were stored on ice, packed with frozen sealed reusable refrigerant packs (e.g., “blue ice”), or refrigerated at 4°C prior to extraction and analysis. Samples were protected using bubble pack bags and extra packing inside the ice chests to prevent breakage during shipping. Ice chests were strapped with shipping tape to keep them from opening during shipment. Samples were shipped to the analytical laboratory by overnight carrier (typically by FedEx), accompanied by a chain of custody. Occasionally during the project, composite samples needed to be split into two different containers and shipped to two different laboratories for analysis.

B.2.5 Holding Times

Holding times for NDMA samples were met by all participating laboratories. Wastewater influent samples were extracted within 7 days, in keeping with the method currently used at the Orange County Sanitation District. The holding time for all other preserved samples was 14 days. Typically, sample extraction was performed within 3 days of sampling. Exceptions include nonpotable samples collected from two utilities where extraction and analysis were performed 6 days after sampling, as noted in the text (Chapter 7).

B.3 ANALYTICAL METHODS

Both LACSD and OCSD analyzed a number of samples for NDMA and NDMA precursors as an in-kind contribution to the project, including all samples collected from wastewater influent or from secondary effluent. A combination of research funds and in-kind contributions from UC Berkeley and OCWD provided for the remainder of the NDMA and NDMA precursor test analyses. All DMA analyses were performed at UC Berkeley. Additional water quality parameters were analyzed at participating utilities or at OCWD as an in-kind contribution to the project.

B.3.1 NDMA Extraction and Analysis

Participating laboratories used variations of the same extraction and analytical procedures for extracting and analyzing NDMA. Laboratory methods described in this section are within the guidelines presented by CalDHS (CalDHS, 2005a). At OCWD, a liquid-liquid extraction technique is used. A 100-g mass of NaCl is added to approximately 1 L of sample volume in a 2-L separatory funnel. The surrogate standard (NDMA-d6) is added, and a laboratory-fortified blank and sample spike are prepared. Three 60-mL aliquots of methylene chloride are then sequentially added to extract the NDMA. The samples are shaken for 2 min and left to separate for 10 min. The methylene chloride layer is then extracted, placed in a 250-mL flask with 7 g of sodium sulfate, and then concentrated to 1 mL using a Zymark concentrator (9 psi nitrogen gas; water bath at 35°C).

OCWD uses an ion trap GC/MS method with methanol and methanol chemical ionization and NDMA-d6 isotopic dilution surrogate standard. The column is 60 m long, in order to decrease the interference of the surrogate standard with NDMA (which would lead to inflated recoveries). Each run time is approximately 20 min. During method development and testing, NDMA recovery ranged from 70 to 130%. The method detection limit (MDL) was approximately 0.34 ng/L.

At OCSD, extraction procedures are similar. The surrogate standard is added to an approximately 1-L sample volume. Extraction with methylene chloride follows at a pH between 5 and 9, using a separatory funnel. The extract is concentrated using rotoevaporation and nitrogen gas. OCSD also uses an ion trap and chemical ionization and mass spectrometry to separate NDMA from the rest of the sample extract. The MDL is 10 ng/L.

At LACSD, samples are spiked with 50 ppb of NDMA-d6 prior to continuous liquid-liquid extraction with methylene chloride. Extracts are then concentrated using an S-EVAP concentrator assembly (manufactured by Organomation Associates, Inc.), reduced to a 1-mL final volume on an N-EVAP system (also manufactured by Organomation Associates, Inc.), and cooled by nitrogen at 35°C. Extracted samples are then analyzed using GC/MS followed by chemical ionization with ammonia.

Antifreeze samples and radiator hoses were purchased from local auto supply stores. Used antifreeze samples were obtained by pipetting directly from the radiators of vehicles or from waste coolant storage drums. The length of time the coolants were used was not determined for any of the samples used in this study. Because of difficulties experienced in reducing the final concentrate volumes to 1 ml, only 10% of the normal 1-L sample was extracted in this study. This problem was caused by the high concentration of glycols in the methylene chloride phase of the extract.

B.3.2 NDMA Precursor Test Procedures

NDMA precursors were measured using the NDMA precursor test, which consisted of exposing the wastewater sample to a relatively high concentration of monochloramine (e.g., 30 mg/L) for 5 days. Samples then typically contained a residual monochloramine concentration between 10 and 15 mg/L. Samples were diluted if necessary and analyzed for NDMA using the procedures detailed above. More details on method development and reproducibility have been presented by Mitch et al. (2003a).

The NDMA precursor test is similar in concept to the THM formation potential test (APHA, 1998). The test was developed by researchers at UC Berkeley to quantify bulk organic nitrogen precursors without determining which nitrogen compounds are actually present and the reactivity of each one with chloramines to form NDMA. Since an excess of chloramines is added, the NDMA reaction is limited by organic nitrogen precursors. The NDMA-FP test is useful for comparing the amount of NDMA precursors in different water samples with each other regardless of actual chlorination conditions. Typical NDMA precursor concentrations measured in untreated wastewater ranged from 1000 to 10,000 ng/L (Mitch et al., 2003a).

B.3.3 Other Water Quality Analyses

DMA analyses were performed at UC Berkeley using high-performance liquid chromatography following derivitization, according to the protocol published by Mitch and Sedlak (2002a). Other water quality parameters of interest were analyzed in accordance with standard methods described by the American Public Health Association, including ammonia (method 4500-NH_3 C), nitrate (method 4500-NO_3^-), nitrite (method 4500-NO_2 B), total organic carbon (method 5310 B), and dissolved organic carbon (method 5310 C) (APHA, 1998).

B.3.4 Quality Assurance and Quality Control Procedures

The following procedures were performed to ensure the quality of analytical results: the use of laboratory blanks and field blanks, the use of NDMA-d6 in all samples as a surrogate to assess percent recovery, analysis of 10% or more duplicate samples, and interlaboratory comparison testing of NDMA and NDMA precursor results.

Dimethylamine analyses were conducted in duplicate for 10% or more samples. Duplicate samples showed good agreement, ranging from 5 to 20%; a higher percent deviation was generally due to very low levels of dimethylamine (>1 µg/L) (Table B-1).

Table B-1. Comparison of Duplicate DMA Results

Location	Facility	Date	DMA, ng/L	DMA Duplicate, ng/L	% Difference
Final Effluent	Whittier Narrows	3/24/2004	3.4	3.6	6
Influent	WF21	12/15/2002	2.5	3	17
Influent	WF21	12/16/2002	0.7	0.91	23
Influent	WF21	1/5/2003	2.2	2.7	19
Influent	WF21	1/8/2003	<0.55	<0.75	--
Influent	WF21	1/28/2003	0.7	1	30
Influent	WF21	1/30/2003	0.63	0.57	10
MF Influent	WF21	1/24/2004	7.5	8	6

NDMA analyses were also analyzed in duplicate. Results are shown in Table B-2. Percent variability between duplicate samples ranged from 10% to almost 30%. Higher variability was seen in untreated wastewater samples.

Table B-2. Comparison of Duplicate NDMA Results

Location	Facility	Date	NDMA, ng/L	NDMA Duplicate, ng/L	% Difference
Influent	San Jose Wastewater	11/17/2002	62.3	69.7	11
Influent	San Jose Wastewater	11/20/2002	304	413	26
RO Product	WF21	5/1/2003	26	29	10

A smaller percentage of NDMA duplicates were analyzed by each utility because of sample volume constraints. Since it is easier to analyze NDMA precursors in duplicate (high NDMA concentrations require more dilution to fall within the calibration range), NDMA precursors were analyzed in duplicate in order to meet project QA/QC guidelines. Results for duplicate NDMA precursors are shown in Table B-3.

Table B-3. Comparison of Duplicate NDMA Precursor Test Results

Location	Facility	Date	NDMA Precursors, ng/L	NDMA Precursors Duplicate, ng/L	% Difference
Influent	WF21	12/11/2002	1355	1510	10
Influent	WF21	12/15/2002	1526	1560	2
Influent	WF21	1/7/2003	1437	1500	4
MF Influent	WF21	12/11/2002	1750	1850	5
MF Influent	WF21	12/15/2002	1350	1370	1
MF Influent	WF21	1/7/2003	2403	2500	4
MF Influent	WF21	4/10/2003	1960	2000	2
MF Effluent	WF21	12/11/2002	95	200	53
MF Effluent	WF21	12/15/2002	377	400	6
MF Effluent	WF21	1/7/2003	892	990	10
MF Effluent	WF21	5/1/2003	1120	1130	1
RO Product	WF21	12/11/2002	13	55	76
RO Product	WF21	12/15/2002	5	18	72
RO Product	WF21	4/10/2003	20	24	17
UV Effluent	WF21	12/11/2002	6.1	8.9	31
UV Effluent	WF21	12/15/2002	7.4	9.6	23
UV Effluent	WF21	5/1/2003	2.5	4.1	39

For water with appreciable NDMA precursor concentrations (i.e., >1000 ng/L), duplicate analyses for NDMA precursors agreed within 10%. In water quality that had <100 ng/L of NDMA precursors (typically only found in reverse osmosis effluent), percent variability between duplicates increased to as much as 72%; however, the absolute difference between duplicate samples was still low (typically less then 10 ng/L and consistently less than 100 ng/L).

An interlaboratory study was conducted on several different sampling dates to assess potential variability associated with shipping, handling, and different laboratory analysis methods. Results are shown in Table B-4.

Table B-4. Results from Interlaboratory Comparison of NDMA Analyses

Facility	Location	Date	NDMA (LACSD Analysis)	NDMA (OCWD Analysis)	% Difference
Inland Empire	Primary	4/7/2003	6.64	7.8	15
San Jose Creek West	Primary	3/23/2004	24	33	27
San Jose Creek West	Primary	3/24/2004	33	11	67
Whittier Narrows	Primary	3/23/2004	790	8.6	99
Whittier Narrows	Primary	3/24/2004	520	24	95
Inland Empire	Secondary	4/7/2003	2.58	2	22
San Jose Creek West	Secondary	3/23/2004	110	70	36
San Jose Creek West	Secondary	3/24/2004	86	81	6
Whittier Narrows	Secondary	3/23/2004	63	53	16
Whittier Narrows	Secondary	3/24/2004	83	60	28
San Jose Creek West	Final	3/23/2004	820	1240	34
San Jose Creek West	Final	3/24/2004	1120	3180	65
Whittier Narrows	Final	3/23/2004	220	144	35
Whittier Narrows	Final	3/24/2004	250	151	40

As with duplicate NDMA analyses, the greatest variability was seen in untreated wastewater or primary effluent samples. Because OCWD has not developed methods for analysis of untreated wastewater and primary effluent samples, all of these analyses were conducted at either LACSD or OCSD. (OCSD did not participate in the interlaboratory testing.) The variability seen during interlaboratory testing indicates some of the analytical challenges of conducting nitrosamine research and underscores the care that must be taken with QA/QC procedures to ensure that the data are meaningful, especially in complex matrices such as untreated wastewater.

APPENDIX C

ANALYTICAL DATA

C.1 SUMMARY

All analytical data that were collected during the project were compiled into a central database that was maintained throughout the project by Malcolm Pirnie. Sample data were collected to address Tasks 2 through 4. Samples were collected from a total of 37 locations at nine different wastewater treatment facilities. The samples were analyzed for NDMA and NDMA precursors. Results are summarized in Table C-1. Samples were also analyzed for other water quality parameters as needed (Table C-2).

During 2004, additional samples were collected to assess the occurrence of NDMA and NDMA precursors in nonpotable water reuse systems. Approximately 50 samples were collected from six different treatment facilities or nonpotable distribution systems during this addendum to the project. Sample results are summarized in Table C-3. Composite samples were also collected from nonchlorinated secondary or tertiary (filtered) effluent at five different wastewater treatment facilities. These samples were shipped to UC Berkeley for laboratory chlorination and/or chloramination bench-scale studies, as summarized in Table C-4. Data quality was ensured by the use of field and laboratory quality assurance/quality control procedures and interlaboratory comparison testing, as described in Appendix B.

Table C-1. Summary of NDMA and NDMA Precursors

Location	Laboratory	Facility	Start Date	Start Day	NDMA, ng/L	NDMA (Filtered), ng/L	NDMA Precursors, ng/L	NDMA Precursors (Filtered), ng/L	Dimethylamine, μg/L
Primary	LACSD	San Jose Creek West	8/26/2002	Thursday			206	39.5	
Secondary	LACSD	San Jose Creek West	8/26/2002	Thursday	362		728	580	
Primary	LACSD	San Jose Creek West	8/29/2002	Sunday	190		2667	96.9	
Secondary	LACSD	San Jose Creek West	8/29/2002	Sunday	5.8		746	15.8	
Influent	OCSD	Plant 1	9/27/2002	Friday	82		5257	8589	79
Influent	OCSD	Plant 1	9/30/2002	Monday	179		4565	8774	82
Influent	OCSD	Plant 1	10/1/2002	Tuesday	83		5574	9793	78
Influent	OCSD	Plant 1	10/2/2002	Wednesday	88		4802	9544	82
Influent	OCSD	San Jose Wastewater	11/17/2002	Sunday	66*		5230	10000	
Influent	UCB	San Jose Wastewater	11/17/2002	Sunday					69.8
Secondary	OCSD	San Jose Wastewater	11/17/2002	Sunday	66.8		684	567	
Secondary	UCB	San Jose Wastewater	11/17/2002	Sunday					1.5
Influent	OCSD	San Jose Wastewater	11/18/2002	Monday	166		3940	12600	
Influent	UCB	San Jose Wastewater	11/18/2002	Monday					91.7
Secondary	OCSD	San Jose Wastewater	11/18/2002	Monday	45.9		1020	1080	
Secondary	UCB	San Jose Wastewater	11/18/2002	Monday					1.4
Influent	OCSD	San Jose Wastewater	11/19/2002	Tuesday	177		6470	9690	
Influent	UCB	San Jose Wastewater	11/19/2002	Tuesday					120
Secondary	OCSD	San Jose Wastewater	11/19/2002	Tuesday	46.7		1280	544	
Secondary	UCB	San Jose Wastewater	11/19/2002	Tuesday					0
Influent	OCSD	San Jose Wastewater	11/20/2002	Wednesday	358.5*		9270	11000	
Influent	UCB	San Jose Wastewater	11/20/2002	Wednesday					107
Secondary	OCSD	San Jose Wastewater	11/20/2002	Wednesday	377		806	805	

* Denotes average concentration of two duplicates or two 12-hr composite samples

Table C-1. Summary of NDMA and NDMA Precursors

Location	Laboratory	Facility	Start Date	Start Day	NDMA, ng/L	NDMA (Filtered), ng/L	NDMA Precursors, ng/L	NDMA Precursors (Filtered), ng/L	Dimethylamine, µg/L
Secondary	UCB	San Jose Wastewater	11/20/2002	Wednesday					1.3
Cl Secondary	LACSD	Whittier Narrows	11/20/2002	Wednesday	76.8	91.8	617.2	580	
Cl Secondary	UCB	Whittier Narrows	11/20/2002	Wednesday					1.4
Influent	LACSD	Whittier Narrows	11/20/2002	Wednesday	54.2	123.2	3351	5067	
Influent	UCB	Whittier Narrows	11/20/2002	Wednesday					68.6
Primary	LACSD	Whittier Narrows	11/20/2002	Wednesday	72.4	124.5	2899	2992	
Primary	UCB	Whittier Narrows	11/20/2002	Wednesday					62.5
Secondary	LACSD	Whittier Narrows	11/20/2002	Wednesday	47.9	33.9	1995	774.3	
Secondary	UCB	Whittier Narrows	11/20/2002	Wednesday					1
Influent	OCWD	WF21	12/11/2002	Wednesday	155		1432.5*		
Influent	UCB	WF21	12/11/2002	Wednesday					2.75*
MF Effluent	OCWD	WF21	12/11/2002	Wednesday	105		147.5*		
MF Effluent	UCB	WF21	12/11/2002	Wednesday					13
MF Influent	OCWD	WF21	12/11/2002	Wednesday	100		1800*		
MF Influent	UCB	WF21	12/11/2002	Wednesday					12
RO Product	OCWD	WF21	12/11/2002	Wednesday	42		34*		
RO Product	UCB	WF21	12/11/2002	Wednesday					0.5
UV Effluent	OCWD	WF21	12/11/2002	Wednesday	2.8		7.5*		
Influent	OCWD	WF21	12/15/2002	Sunday	34		1543*		
Influent	UCB	WF21	12/15/2002	Sunday					0.805*
MF Effluent	OCWD	WF21	12/15/2002	Sunday	23		388.5*		
MF Effluent	UCB	WF21	12/15/2002	Sunday					8.25*

* Denotes average concentration of two duplicates or two 12-hr composite samples

Table C-1. Summary of NDMA and NDMA Precursors

Location	Laboratory	Facility	Start Date	Start Day	NDMA, ng/L	NDMA (Filtered), ng/L	NDMA Precursors, ng/L	NDMA Precursors (Filtered), ng/L	Dimethylamine, µg/L
MF Influent	OCWD	WF21	12/15/2002	Sunday	20		1360*		
MF Influent	UCB	WF21	12/15/2002	Sunday					7.2*
RO Product	OCWD	WF21	12/15/2002	Sunday	13		11.5*		
UV Effluent	OCWD	WF21	12/15/2002	Sunday	2.2		8.5*		
Influent	UCB	WF21	1/5/2003	Sunday					2.45*
MF Effluent	UCB	WF21	1/5/2003	Sunday					11.2
MF Influent	UCB	WF21	1/5/2003	Sunday					10.6
UV Effluent	UCB	WF21	1/5/2003	Sunday					0.7
Control	OCWD	WF21	1/7/2003	Tuesday	18		79*		
Influent	OCWD	WF21	1/7/2003	Tuesday	63		1468.5*		
MF Effluent	OCWD	WF21	1/7/2003	Tuesday	98		941*		
MF Effluent	UCB	WF21	1/7/2003	Tuesday					3.4
MF Influent	OCWD	WF21	1/7/2003	Tuesday	97		2451.5*		
MF Influent	UCB	WF21	1/7/2003	Tuesday					2.6
RO Product	OCWD	WF21	1/7/2003	Tuesday	49		40		
UV Effluent	OCWD	WF21	1/7/2003	Tuesday	28		16		
Industrial Waste	OCSD	Pioneer Circuit (DTC)	1/27/2003	Monday	4225*		82730*	86535*	
Industrial Waste	UCB	Pioneer Circuit (DTC)	1/27/2003	Monday					1242*
Influent	OCWD	WF21	1/28/2003	Tuesday	38		1100		
Influent	UCB	WF21	1/28/2003	Tuesday					0.85*
MF Effluent	OCWD	WF21	1/28/2003	Tuesday	43		143		
MF Effluent	UCB	WF21	1/28/2003	Tuesday					7.8
MF Influent	OCWD	WF21	1/28/2003	Tuesday	33		1240		

* Denotes average concentration of two duplicates or two 12-hr composite samples

Table C-1. Summary of NDMA and NDMA Precursors

Location	Laboratory	Facility	Start Date	Start Day	NDMA, ng/L	NDMA (Filtered), ng/L	NDMA Precursors, ng/L	NDMA Precursors (Filtered), ng/L	Dimethylamine, µg/L
MF Influent	UCB	WF21	1/28/2003	Tuesday					1.9*
RO Product	OCWD	WF21	1/28/2003	Tuesday	17		52		
UV Effluent	OCWD	WF21	1/28/2003	Tuesday	16		27		
UV Effluent	UCB	WF21	1/28/2003	Tuesday					0.9
Secondary	OCSD	Cirtech Industry (non-DTC)	1/30/2003	Thursday	28.75*		1570*	1936.5*	
Secondary	UCB	Cirtech Industry (non-DTC)	1/30/2003	Thursday					7.2*
Influent	OCWD	WF21	1/30/2003	Thursday	60		1260		
Influent	UCB	WF21	1/30/2003	Thursday					0.6*
MF Effluent	OCWD	WF21	1/30/2003	Thursday	76		1230		
MF Effluent	UCB	WF21	1/30/2003	Thursday					3.8
MF Influent	OCWD	WF21	1/30/2003	Thursday	71		1390		
MF Influent	UCB	WF21	1/30/2003	Thursday					3.6
RO Product	OCWD	WF21	1/30/2003	Thursday	25		50		
UV Effluent	OCWD	WF21	1/30/2003	Thursday	3.3		18		
Trunkline	OCSD	Residential (non-DTC)	3/20/2003	Thursday	27.1		10700	11200	
Trunkline	UCB	Residential (non-DTC)	3/20/2003	Thursday					92
Trunkline	OCSD	Residential (non-DTC)	3/21/2003	Friday	39.85*		8145*	9595*	
Trunkline	UCB	Residential (non-DTC)	3/21/2003	Friday					76.5*
Filter Backwash	LACSD	Inland Empire Reclamation Plant 1	4/7/2003	Monday	191		97		
Final	LACSD	Inland Empire	4/7/2003	Monday	16.5		131		

* Denotes average concentration of two duplicates or two 12-hr composite samples

Table C-1. Summary of NDMA and NDMA Precursors

Location	Laboratory	Facility	Start Date	Start Day	NDMA, ng/L	NDMA (Filtered), ng/L	NDMA Precursors, ng/L	NDMA Precursors (Filtered), ng/L	Dimethylamine, µg/L
		Reclamation Plant 1							
Primary	LACSD	Inland Empire Reclamation Plant 1	4/7/2003	Monday	6.64	5.73	2497	2569	
Primary	OCWD	Inland Empire Reclamation Plant 1	4/7/2003	Monday	7.8				
Primary	UCB	Inland Empire Reclamation Plant 1	4/7/2003	Monday					57
Secondary	LACSD	Inland Empire Reclamation Plant 1	4/7/2003	Monday	2.58	2.78	664	659	
Secondary	UCB	Inland Empire Reclamation Plant 1	4/7/2003	Monday					0.57
Influent	OCWD	WF21	4/10/2003	Thursday	36		1400		
MF Effluent	OCWD	WF21	4/10/2003	Thursday	46		1730		
MF Influent	OCWD	WF21	4/10/2003	Thursday	42		1980*		
RO Product	OCWD	WF21	4/10/2003	Thursday	19		22*		
UV Effluent	OCWD	WF21	4/10/2003	Thursday	1.6		6.1		
Influent	OCWD	WF21	5/1/2003	Thursday	36		970		
MF Effluent	OCWD	WF21	5/1/2003	Thursday	62		1125*		
MF Influent	OCWD	WF21	5/1/2003	Thursday	42		1680		
RO Product	OCWD	WF21	5/1/2003	Thursday	27.5*		52		
UV Effluent	OCWD	WF21	5/1/2003	Thursday	1.4		3.3*		
Trunkline	OCSD	Residential (DTC) - After	5/5/2003	Monday	88		480	1000	
Trunkline	UCB	Residential (DTC) - After	5/5/2003	Monday					172

* Denotes average concentration of two duplicates or two 12-hr composite samples

Table C-1. Summary of NDMA and NDMA Precursors

Location	Laboratory	Facility	Start Date	Start Day	NDMA, ng/L	NDMA (Filtered), ng/L	NDMA Precursors, ng/L	NDMA Precursors (Filtered), ng/L	Dimethylamine, µg/L
Trunkline	OCSD	Residential (DTC) - Before	5/5/2003	Monday	150		580	57	
Trunkline	UCB	Residential (DTC) - Before	5/5/2003	Monday					64
Trunkline	OCSD	Residential (DTC) - During	5/5/2003	Monday	2400		89000	48000	
Trunkline	UCB	Residential (DTC) - During	5/5/2003	Monday					51
Final	OCWD	San Jose Wastewater	9/15/2003	Monday	15		2250		
Final	UCB	San Jose Wastewater	9/15/2003	Monday					0.7
Influent	UCB	San Jose Wastewater	9/15/2003	Monday					76
Postfiltration	OCWD	San Jose Wastewater	9/15/2003	Monday	18		1640		
Postfiltration	UCB	San Jose Wastewater	9/15/2003	Monday					2.3
Primary	UCB	San Jose Wastewater	9/15/2003	Monday					94
Secondary	LACSD	San Jose Wastewater	9/15/2003	Monday	32.6	30.9	219	247	
Secondary	UCB	San Jose Wastewater	9/15/2003	Monday					1
Final	OCWD	San Jose Wastewater	9/16/2003	Tuesday	16		1370		
Final	UCB	San Jose Wastewater	9/16/2003	Tuesday					0.37
Influent	LACSD	San Jose Wastewater	9/16/2003	Tuesday	35.3		298	6270	
Influent	UCB	San Jose Wastewater	9/16/2003	Tuesday					78
Postfiltration	OCWD	San Jose Wastewater	9/16/2003	Tuesday	20		920		
Postfiltration	UCB	San Jose Wastewater	9/16/2003	Tuesday					5.2
Primary	LACSD	San Jose Wastewater	9/16/2003	Tuesday	31.4	27.9	4130	6390	

* Denotes average concentration of two duplicates or two 12-hr composite samples

Table C-1. Summary of NDMA and NDMA Precursors

Location	Laboratory	Facility	Start Date	Start Day	NDMA, ng/L	NDMA (Filtered), ng/L	NDMA Precursors, ng/L	NDMA Precursors (Filtered), ng/L	Dimethylamine, µg/L
Primary	UCB	San Jose Wastewater	9/16/2003	Tuesday					110
Secondary	LACSD	San Jose Wastewater	9/16/2003	Tuesday	27.9	33.4	1440	1400	
Secondary	UCB	San Jose Wastewater	9/16/2003	Tuesday					0.97
Final	OCWD	San Jose Wastewater	9/17/2003	Wednesday	26		1040		
Final	UCB	San Jose Wastewater	9/17/2003	Wednesday					0.37
Influent	LACSD	San Jose Wastewater	9/17/2003	Wednesday	104.1	61.9	3190	6760	
Influent	UCB	San Jose Wastewater	9/17/2003	Wednesday					91
Postfiltration	OCWD	San Jose Wastewater	9/17/2003	Wednesday	38		1400		
Postfiltration	UCB	San Jose Wastewater	9/17/2003	Wednesday					7
Primary	LACSD	San Jose Wastewater	9/17/2003	Wednesday	36.9	65	3110	4840	
Primary	UCB	San Jose Wastewater	9/17/2003	Wednesday					120
Secondary	LACSD	San Jose Wastewater	9/17/2003	Wednesday	35.4	40.3	820	810	
Secondary	UCB	San Jose Wastewater	9/17/2003	Wednesday					0.83
Influent	OCSD	Scottsdale Wastewater	9/28/2003	Sunday	130		3400		
Influent	UCB	Scottsdale Wastewater	9/28/2003	Sunday					46
Primary	OCSD	Scottsdale Wastewater	9/28/2003	Sunday	140		3800		
Primary	UCB	Scottsdale Wastewater	9/28/2003	Sunday					48
Secondary	OCSD	Scottsdale Wastewater	9/28/2003	Sunday	37		940		
Secondary	UCB	Scottsdale Wastewater	9/28/2003	Sunday					0.4
Primary	OCSD	Plant 1	9/29/2003	Monday	55		5100		
Secondary	OCSD	Plant 1	9/29/2003	Monday	41		1400		
Primary	OCSD	Plant 2	9/29/2003	Monday	93		8400		
Secondary	OCSD	Plant 2	9/29/2003	Monday	26		1400		

* Denotes average concentration of two duplicates or two 12-hr composite samples

Table C-1. Summary of NDMA and NDMA Precursors

Location	Laboratory	Facility	Start Date	Start Day	NDMA, ng/L	NDMA (Filtered), ng/L	NDMA Precursors, ng/L	NDMA Precursors (Filtered), ng/L	Dimethylamine, µg/L
Influent	OCSD	Scottsdale Wastewater	9/29/2003	Monday	51		2800		
Influent	UCB	Scottsdale Wastewater	9/29/2003	Monday					43
Primary	OCSD	Scottsdale Wastewater	9/29/2003	Monday	73		3600		
Primary	UCB	Scottsdale Wastewater	9/29/2003	Monday					43
Secondary	OCSD	Scottsdale Wastewater	9/29/2003	Monday			860		
Secondary	UCB	Scottsdale Wastewater	9/29/2003	Monday					0.39
Primary	OCSD	Plant 1	9/30/2003	Tuesday	82		4700		
Secondary	OCSD	Plant 1	9/30/2003	Tuesday	83		1400		
Primary	OCSD	Plant 2	9/30/2003	Tuesday	110		9400		
Secondary	OCSD	Plant 2	9/30/2003	Tuesday	52		1700		
Influent	UCB	Scottsdale Wastewater	9/30/2003	Tuesday					48
Primary	UCB	Scottsdale Wastewater	9/30/2003	Tuesday					44
Secondary	UCB	Scottsdale Wastewater	9/30/2003	Tuesday					0.6
Influent	LACSD	Whittier Narrows	10/21/2003	Tuesday	62.3	37.8	4330	6230	
Primary	LACSD	Whittier Narrows	10/21/2003	Tuesday	14	28	3670	5160	
Secondary	LACSD	Whittier Narrows	10/21/2003	Tuesday	27.5	23.5	1700	1070	
Secondary	LACSD	San Jose Creek West	10/22/2003	Wednesday	34.9	42.4			
Influent	LACSD	Whittier Narrows	10/22/2003	Wednesday	16.7	23.3	1680	2570	
Primary	LACSD	Whittier Narrows	10/22/2003	Wednesday	12.5	20.3			
MF Influent	UCB	WF21	12/24/2003						7.75
Secondary	LACSD	Inland Empire Reclamation Plant 1	3/1/2004	Wednesday	3.1		870		

* Denotes average concentration of two duplicates or two 12-hr composite samples

Table C-1. Summary of NDMA and NDMA Precursors

Location	Laboratory	Facility	Start Date	Start Day	NDMA, ng/L	NDMA (Filtered), ng/L	NDMA Precursors, ng/L	NDMA Precursors (Filtered), ng/L	Dimethylamine, µg/L
Secondary	UCB	Inland Empire Reclamation Plant 1	3/1/2004	Wednesday					0.52
Final	LACSD	San Jose Creek West	3/23/2004	Tuesday	820		2500		
Final	OCWD	San Jose Creek West	3/23/2004	Tuesday	1240		18900		
Final	UCB	San Jose Creek West	3/23/2004	Tuesday					59
Primary	LACSD	San Jose Creek West	3/23/2004	Tuesday	24		1200		
Primary	OCWD	San Jose Creek West	3/23/2004	Tuesday	33		20300		
Primary	UCB	San Jose Creek West	3/23/2004	Tuesday					89
Secondary	LACSD	San Jose Creek West	3/23/2004	Tuesday	110		27100		
Secondary	OCWD	San Jose Creek West	3/23/2004	Tuesday	70		21200		
Secondary	UCB	San Jose Creek West	3/23/2004	Tuesday					46
Cl Secondary	LACSD	Whittier Narrows	3/23/2004	Tuesday	220		640		
Cl Secondary	OCWD	Whittier Narrows	3/23/2004	Tuesday	144		2690		
Primary	LACSD	Whittier Narrows	3/23/2004	Tuesday	790		3000		
Primary	OCWD	Whittier Narrows	3/23/2004	Tuesday	8.6		21000		
Primary	UCB	Whittier Narrows	3/23/2004	Tuesday					114
Secondary	LACSD	Whittier Narrows	3/23/2004	Tuesday	63		2800		
Secondary	OCWD	Whittier Narrows	3/23/2004	Tuesday	53		4910		
Secondary	UCB	Whittier Narrows	3/23/2004	Tuesday					3.6
Final	LACSD	San Jose Creek West	3/24/2004	Wednesday	1120		5400		
Final	OCWD	San Jose Creek West	3/24/2004	Wednesday	3180		16400		
Final	UCB	San Jose Creek West	3/24/2004	Wednesday					51
Primary	LACSD	San Jose Creek West	3/24/2004	Wednesday	33		5400		

* Denotes average concentration of two duplicates or two 12-hr composite samples

Table C-1. Summary of NDMA and NDMA Precursors

Location	Laboratory	Facility	Start Date	Start Day	NDMA, ng/L	NDMA (Filtered), ng/L	NDMA Precursors, ng/L	NDMA Precursors (Filtered), ng/L	Dimethylamine, µg/L
Primary	OCWD	San Jose Creek West	3/24/2004	Wednesday	11		30500		
Primary	UCB	San Jose Creek West	3/24/2004	Wednesday					102
Secondary	LACSD	San Jose Creek West	3/24/2004	Wednesday	86		28900		
Secondary	OCWD	San Jose Creek West	3/24/2004	Wednesday	81		19700		
Secondary	UCB	San Jose Creek West	3/24/2004	Wednesday					60
Cl Secondary	LACSD	Whittier Narrows	3/24/2004	Wednesday	250		910		
Cl Secondary	OCWD	Whittier Narrows	3/24/2004	Wednesday	151		1760		
Cl Secondary	UCB	Whittier Narrows	3/24/2004	Wednesday					4.55*
Primary	LACSD	Whittier Narrows	3/24/2004	Wednesday	520		2400		
Primary	OCWD	Whittier Narrows	3/24/2004	Wednesday	24		21200		
Primary	UCB	Whittier Narrows	3/24/2004	Wednesday					79
Secondary	LACSD	Whittier Narrows	3/24/2004	Wednesday	83		2600		
Secondary	OCWD	Whittier Narrows	3/24/2004	Wednesday	60		3470		
Secondary	UCB	Whittier Narrows	3/24/2004	Wednesday					3.4
Primary	LACSD	Inland Empire Reclamation Plant 1	3/29/2004	Monday	28		5500		
Primary	UCB	Inland Empire Reclamation Plant 1	3/29/2004	Monday					84
Secondary	LACSD	Inland Empire Reclamation Plant 1	3/29/2004	Monday	5.6		820		
Secondary	UCB	Inland Empire Reclamation Plant 1	3/29/2004	Monday					0.54
Primary	LACSD	Inland Empire	3/30/2004	Tuesday	42		5300		

* Denotes average concentration of two duplicates or two 12-hr composite samples

Table C-1. Summary of NDMA and NDMA Precursors

Location	Laboratory	Facility	Start Date	Start Day	NDMA, ng/L	NDMA (Filtered), ng/L	NDMA Precursors, ng/L	NDMA Precursors (Filtered), ng/L	Dimethylamine, µg/L
		Reclamation Plant 1							
Primary	UCB	Inland Empire Reclamation Plant 1	3/30/2004	Tuesday					93
Secondary	LACSD	Inland Empire Reclamation Plant 1	3/30/2004	Tuesday	4.6		900		
Secondary	UCB	Inland Empire Reclamation Plant 1	3/30/2004	Tuesday					0.59
Primary	LACSD	Inland Empire Reclamation Plant 1	3/31/2004	Wednesday	41		4000		
Primary	UCB	Inland Empire Reclamation Plant 1	3/31/2004	Wednesday					71

* Denotes average concentration of two duplicates or two 12-hr composite samples

Table C-2. Summary of Water Quality Parameters

Location	Laboratory	Facility	Start Date	Start Day	Ammonia Nitrogen, mg/L	BOD, mg/L	Cl (Total) mg/L	Dissolved Organic Carbon, mg/L	Kjeldahl Nitrogen, mg/L	Nitrate Nitrogen, mg/L	Nitrite and Nitrate Nitrogen, mg/L
Primary	LACSD	San Jose Creek West	26-Aug-02	Thursday	24			65.4			
Secondary	LACSD	San Jose Creek West	26-Aug-02	Thursday	9.9			7.16		3.42	
Primary	LACSD	San Jose Creek West	29-Aug-02	Sunday	24.2						
Secondary	LACSD	San Jose Creek West	29-Aug-02	Sunday	9.6			7.22		4.39	
Influent	OCSD	Plant 1	27-Sep-02	Friday	29	280					
Influent	OCSD	Plant 1	30-Sep-02	Monday	28	240				0.33	
Influent	OCSD	Plant 1	01-Oct-02	Tuesday	29	280				0.66	
Influent	OCSD	Plant 1	02-Oct-02	Wednesday	30	240				0.85	
Influent	CSJ	San Jose Wastewater	17-Nov-02	Sunday	23.4	260					
Secondary	CSJ	San Jose Wastewater	17-Nov-02	Sunday		9				8.2	
Influent	CSJ	San Jose Wastewater	18-Nov-02	Monday	24.7						
Secondary	CSJ	San Jose Wastewater	18-Nov-02	Monday		10				7.7	
Influent	CSJ	San Jose Wastewater	19-Nov-02	Tuesday	25.2	290					
Secondary	CSJ	San Jose Wastewater	19-Nov-02	Tuesday		10				8.6	
Influent	CSJ	San Jose Wastewater	20-Nov-02	Wednesday	25.5	250					
Secondary	CSJ	San Jose Wastewater	20-Nov-02	Wednesday		7				8.5	
Cl Secondary	LACSD	Whittier Narrows	20-Nov-02	Wednesday	1.1			6.53		4.71	
Influent	LACSD	Whittier Narrows	20-Nov-02	Wednesday	24.2			60.6			
Primary	LACSD	Whittier Narrows	20-Nov-02	Wednesday	25.4			54.2			
Secondary	LACSD	Whittier Narrows	20-Nov-02	Wednesday	1.2			7.46		4.78	
Influent	OCWD	WF21	11-Dec-02	Wednesday	19.8			28.3	22		1.14

Table C-2. Summary of Water Quality Parameters

Location	Laboratory	Facility	Start Date	Start Day	Ammonia Nitrogen, mg/L	BOD, mg/L	Cl (Total) mg/L	Dissolved Organic Carbon, mg/L	Kjeldahl Nitrogen, mg/L	Nitrate Nitrogen, mg/L	Nitrite and Nitrate Nitrogen, mg/L
MF Effluent	OCWD	WF21	11-Dec-02	Wednesday	24			36.6	25.3	0.76	1.02
MF Influent	OCWD	WF21	11-Dec-02	Wednesday	24			27.2	25.5		1.15
RO Product	OCWD	WF21	11-Dec-02	Wednesday	1			10.2			0.12
UV Effluent	OCWD	WF21	11-Dec-02	Wednesday	1		0.9	18.7		0.15	0.18
Influent	OCWD	WF21	15-Dec-02	Sunday	19.1			11.2	21.2		1.18
MF Effluent	OCWD	WF21	15-Dec-02	Sunday	22.4			23.6	25.9		1.09
MF Influent	OCWD	WF21	15-Dec-02	Sunday	23.1			12.2	25.9		1.17
RO Product	OCWD	WF21	15-Dec-02	Sunday	1.2			11.5	1.2		
UV Effluent	OCWD	WF21	15-Dec-02	Sunday	1		0.4	15.2	1.1	0.11	0.14
Control	OCWD	WF21	07-Jan-03	Tuesday							
Influent	OCWD	WF21	07-Jan-03	Tuesday							0.22
MF Effluent	OCWD	WF21	07-Jan-03	Tuesday							0.23
MF Influent	OCWD	WF21	07-Jan-03	Tuesday							0.33
RO Product	OCWD	WF21	07-Jan-03	Tuesday							
UV Effluent	OCWD	WF21	07-Jan-03	Tuesday							
Influent	OCWD	WF21	28-Jan-03	Tuesday	13.3			33.9	14.1		1.09
MF Effluent	OCWD	WF21	28-Jan-03	Tuesday	17.1		0.6	34.3	17.3	0.13	1
MF Influent	OCWD	WF21	28-Jan-03	Tuesday	18.1		2	28.8	18.6		1.02
RO Product	OCWD	WF21	28-Jan-03	Tuesday	0.7		1.7	14.1	0.7		
UV Effluent	OCWD	WF21	28-Jan-03	Tuesday	1		1.7	18.1	1		0.11
Influent	OCWD	WF21	30-Jan-03	Thursday						0.23	1.91
MF Effluent	OCWD	WF21	30-Jan-03	Thursday						0.28	1.82

Table C-2. Summary of Water Quality Parameters

Location	Laboratory	Facility	Start Date	Start Day	Ammonia Nitrogen, mg/L	BOD, mg/L	Cl (Total) mg/L	Dissolved Organic Carbon, mg/L	Kjeldahl Nitrogen, mg/L	Nitrate Nitrogen, mg/L	Nitrite and Nitrate Nitrogen, mg/L
MF Influent	OCWD	WF21	30-Jan-03	Thursday						0.23	1.81
RO Product	OCWD	WF21	30-Jan-03	Thursday							
UV Effluent	OCWD	WF21	30-Jan-03	Thursday						0.12	0.15
Primary	LACSD	Inland Empire Reclamation Plant 1	07-Apr-03	Monday	23.7			90.4			
Secondary	LACSD	Inland Empire Reclamation Plant 1	07-Apr-03	Monday				8.19		6.43	
Influent	OCWD	WF21	10-Apr-03	Thursday	19.3			12	20.7		0.3
MF Effluent	OCWD	WF21	10-Apr-03	Thursday	18.1		0.4	10.8	19.1	0.14	0.7
MF Influent	OCWD	WF21	10-Apr-03	Thursday	19.4		2.1	12.7	20.8		0.37
RO Product	OCWD	WF21	10-Apr-03	Thursday	0.7		1.9	0.3	0.7		
UV Effluent	OCWD	WF21	10-Apr-03	Thursday	0.6		1.3	0.3	0.7		
Influent	OCWD	WF21	01-May-03	Thursday	21.5			11.1	23.4		1.023
MF Effluent	OCWD	WF21	01-May-03	Thursday	21.5		1.8	9.9	22.7	0.32	0.75
MF Influent	OCWD	WF21	01-May-03	Thursday	22		4.8	12.3	24.3		0.917
RO Product	OCWD	WF21	01-May-03	Thursday	1.1		3.9	0.2	1.2	0.37	0.37
UV Effluent	OCWD	WF21	01-May-03	Thursday	1		2.1	0.23	1.1	0.42	0.42
Secondary	LACSD	Inland Empire Reclamation Plant 1	01-Mar-04	Wednesday				5.1			
Final	LACSD	San Jose Creek West	23-Mar-04	Tuesday	2.8			5.1		5.86	
Primary	LACSD	San Jose Creek West	23-Mar-04	Tuesday	24			41			
Secondary	LACSD	San Jose Creek West	23-Mar-04	Tuesday	1.8			5.3		5.44	

Table C-2. Summary of Water Quality Parameters

Location	Laboratory	Facility	Start Date	Start Day	Ammonia Nitrogen, mg/L	BOD, mg/L	Cl (Total) mg/L	Dissolved Organic Carbon, mg/L	Kjeldahl Nitrogen, mg/L	Nitrate Nitrogen, mg/L	Nitrite and Nitrate Nitrogen, mg/L
Cl Secondary	LACSD	Whittier Narrows	23-Mar-04	Tuesday	0.9			70		6.38	
Primary	LACSD	Whittier Narrows	23-Mar-04	Tuesday	27.2			42			
Secondary	LACSD	Whittier Narrows	23-Mar-04	Tuesday	0.9			5.8		6.28	
Final	LACSD	San Jose Creek West	24-Mar-04	Wednesday	6.5			5.6		4.5	
Primary	LACSD	San Jose Creek West	24-Mar-04	Wednesday	25.6			40			
Secondary	LACSD	San Jose Creek West	24-Mar-04	Wednesday	5.4			5.5		4.35	
Cl Secondary	LACSD	Whittier Narrows	24-Mar-04	Wednesday	1.1			6.3		5.72	
Primary	LACSD	Whittier Narrows	24-Mar-04	Wednesday	25.2			70			
Secondary	LACSD	Whittier Narrows	24-Mar-04	Wednesday	1.1			6.2		5.34	
Primary	LACSD	Inland Empire Reclamation Plant 1	29-Mar-04	Monday	33.4			36			
Secondary	LACSD	Inland Empire Reclamation Plant 1	29-Mar-04	Monday				5.6			
Primary	LACSD	Inland Empire Reclamation Plant 1	30-Mar-04	Tuesday	24.6			42			
Secondary	LACSD	Inland Empire Reclamation Plant 1	30-Mar-04	Tuesday				5.4			
Primary	LACSD	Inland Empire Reclamation Plant 1	31-Mar-04	Wednesday	26.7			35			

Table C-2. Summary of Water Quality Parameters

Location	Laboratory	Facility	Start Date	Start Day	Nitrite Nitrogen, mg/L	Organic Nitrogen, mg/L	pH	Total Alkalinity, mg/L	Total Organic Carbon, mg/L	Total Suspended Solids, mg/L
Primary	LACSD	San Jose Creek West	26-Aug-02	Thursday	0.011	9				88
Secondary	LACSD	San Jose Creek West	26-Aug-02	Thursday	0.28	1.5				10
Primary	LACSD	San Jose Creek West	29-Aug-02	Sunday		8.3				86
Secondary	LACSD	San Jose Creek West	29-Aug-02	Sunday	0.27	1.6				
Influent	OCSD	Plant 1	27-Sep-02	Friday		43.3				270
Influent	OCSD	Plant 1	30-Sep-02	Monday	0.01	42.3				264
Influent	OCSD	Plant 1	01-Oct-02	Tuesday	0.01	49				284
Influent	OCSD	Plant 1	02-Oct-02	Wednesday	0.06	40				258
Influent	CSJ	San Jose Wastewater	17-Nov-02	Sunday		40.4				260
Secondary	CSJ	San Jose Wastewater	17-Nov-02	Sunday	0.05	1.2				11
Influent	CSJ	San Jose Wastewater	18-Nov-02	Monday		43.4				360
Secondary	CSJ	San Jose Wastewater	18-Nov-02	Monday	0.05	6.4				9
Influent	CSJ	San Jose Wastewater	19-Nov-02	Tuesday		40.3				260
Secondary	CSJ	San Jose Wastewater	19-Nov-02	Tuesday	0.08	4.8				11
Influent	CSJ	San Jose Wastewater	20-Nov-02	Wednesday		41.1				340
Secondary	CSJ	San Jose Wastewater	20-Nov-02	Wednesday	0.05	2.7				10
Cl Secondary	LACSD	Whittier Narrows	20-Nov-02	Wednesday		1.4				
Influent	LACSD	Whittier Narrows	20-Nov-02	Wednesday		11.7				228
Primary	LACSD	Whittier Narrows	20-Nov-02	Wednesday		9.8				110
Secondary	LACSD	Whittier Narrows	20-Nov-02	Wednesday		1.5				

Table C-2. Summary of Water Quality Parameters

Location	Laboratory	Facility	Start Date	Start Day	Nitrite Nitrogen, mg/L	Organic Nitrogen, mg/L	pH	Total Alkalinity, mg/L	Total Organic Carbon, mg/L	Total Suspended Solids, mg/L
Influent	OCWD	WF21	11-Dec-02	Wednesday	1.135	2.2	8	231	32.5	
MF Effluent	OCWD	WF21	11-Dec-02	Wednesday	0.259	1.3		65.5	37.5	
MF Influent	OCWD	WF21	11-Dec-02	Wednesday	1.152	1.5		234	27.9	
RO Product	OCWD	WF21	11-Dec-02	Wednesday	0.02	1		5	11.2	
UV Effluent	OCWD	WF21	11-Dec-02	Wednesday	0.03	1		4.2	18.1	
Influent	OCWD	WF21	15-Dec-02	Sunday	1.18	2.1		236	11.9	
MF Effluent	OCWD	WF21	15-Dec-02	Sunday	1.003	3.5		85.2	24.4	
MF Influent	OCWD	WF21	15-Dec-02	Sunday	1.17	2.7		231	14.3	
RO Product	OCWD	WF21	15-Dec-02	Sunday	0.027			5.2	11.3	
UV Effluent	OCWD	WF21	15-Dec-02	Sunday	0.032			4.6	15.2	
Control	OCWD	WF21	07-Jan-03	Tuesday				2.5	0.13	
Influent	OCWD	WF21	07-Jan-03	Tuesday	0.17			246		11
MF Effluent	OCWD	WF21	07-Jan-03	Tuesday	0.162			105		
MF Influent	OCWD	WF21	07-Jan-03	Tuesday	0.262			250		5.6
RO Product	OCWD	WF21	07-Jan-03	Tuesday	0.002			5.8	11.1	
UV Effluent	OCWD	WF21	07-Jan-03	Tuesday	0.025			2.7	17.6	
Influent	OCWD	WF21	28-Jan-03	Tuesday	1.04	0.8		255	34.9	3.3
MF Effluent	OCWD	WF21	28-Jan-03	Tuesday	0.864	0.2		115	34.8	
MF Influent	OCWD	WF21	28-Jan-03	Tuesday	1.011	0.4		255	30.3	2.8
RO Product	OCWD	WF21	28-Jan-03	Tuesday	0.028			12.4	14.3	
UV Effluent	OCWD	WF21	28-Jan-03	Tuesday	0.023			10.8	18	
Influent	OCWD	WF21	30-Jan-03	Thursday	1.68			251	15.5	3.7

Table C-2. Summary of Water Quality Parameters

Location	Laboratory	Facility	Start Date	Start Day	Nitrite Nitrogen, mg/L	Organic Nitrogen, mg/L	pH	Total Alkalinity, mg/L	Total Organic Carbon, mg/L	Total Suspended Solids, mg/L
MF Effluent	OCWD	WF21	30-Jan-03	Thursday	1.54			107	16.9	
MF Influent	OCWD	WF21	30-Jan-03	Thursday	1.58			253	18.8	3.6
RO Product	OCWD	WF21	30-Jan-03	Thursday	0.052			10.4	3.77	
UV Effluent	OCWD	WF21	30-Jan-03	Thursday	0.033			7.3	8.5	1
Primary	LACSD	Inland Empire Reclamation Plant 1	07-Apr-03	Monday		10.3				124
Secondary	LACSD	Inland Empire Reclamation Plant 1	07-Apr-03	Monday		1.8				
Influent	OCWD	WF21	10-Apr-03	Thursday	0.303	1.4		259	13.7	4
MF Effluent	OCWD	WF21	10-Apr-03	Thursday	0.554	1		132	11	
MF Influent	OCWD	WF21	10-Apr-03	Thursday	0.371	1.4		259	14.6	3.8
RO Product	OCWD	WF21	10-Apr-03	Thursday				42	1.3	
UV Effluent	OCWD	WF21	10-Apr-03	Thursday				11.2	0.4	
Influent	OCWD	WF21	01-May-03	Thursday	1.023	1.9	8	277	13.2	5.4
MF Effluent	OCWD	WF21	01-May-03	Thursday	0.427	1.2		129	10.2	
MF Influent	OCWD	WF21	01-May-03	Thursday	0.917	2.3		277	14.7	7.8
RO Product	OCWD	WF21	01-May-03	Thursday		0.1		11	0.7	
UV Effluent	OCWD	WF21	01-May-03	Thursday				9.6	0.35	
Secondary	LACSD	Inland Empire Reclamation Plant 1	01-Mar-04	Wednesday		1.5				4
Final	LACSD	San Jose Creek West	23-Mar-04	Tuesday	0.07	1.6				
Primary	LACSD	San Jose Creek West	23-Mar-04	Tuesday		10.5				95
Secondary	LACSD	San Jose Creek West	23-Mar-04	Tuesday	0.3	1.4				
Cl Secondary	LACSD	Whittier Narrows	23-Mar-04	Tuesday	0.05	1.6				

Table C-2. Summary of Water Quality Parameters

Location	Laboratory	Facility	Start Date	Start Day	Nitrite Nitrogen, mg/L	Organic Nitrogen, mg/L	pH	Total Alkalinity, mg/L	Total Organic Carbon, mg/L	Total Suspended Solids, mg/L
Primary	LACSD	Whittier Narrows	23-Mar-04	Tuesday		8.5				7
Secondary	LACSD	Whittier Narrows	23-Mar-04	Tuesday	0.15	1.4				
Final	LACSD	San Jose Creek West	24-Mar-04	Wednesday	0.11	4.5				2
Primary	LACSD	San Jose Creek West	24-Mar-04	Wednesday		8.8				62
Secondary	LACSD	San Jose Creek West	24-Mar-04	Wednesday	0.19	1.5				2
Cl Secondary	LACSD	Whittier Narrows	24-Mar-04	Wednesday	0.2	1.6				1
Primary	LACSD	Whittier Narrows	24-Mar-04	Wednesday		8.6				80
Secondary	LACSD	Whittier Narrows	24-Mar-04	Wednesday	0.35	1.5				3
Primary	LACSD	Inland Empire Reclamation Plant 1	29-Mar-04	Monday		7.6				51
Secondary	LACSD	Inland Empire Reclamation Plant 1	29-Mar-04	Monday		1.9				4
Primary	LACSD	Inland Empire Reclamation Plant 1	30-Mar-04	Tuesday		7.2				55
Secondary	LACSD	Inland Empire Reclamation Plant 1	30-Mar-04	Tuesday		1.7				3
Primary	LACSD	Inland Empire Reclamation Plant 1	31-Mar-04	Wednesday		6.6				48

Table C-3. Summary of Nonpotable Study Field Data

Utility	Sample ID	Sample Location	Sample Type	Sample Date	NDMA, ng/L	NDMA Precursors, ng/L	Free Chlorine, mg/L	Total Chlorine, mg/L	TOC, mg/L	DOC, mg/L	Nitrite, mg/L
System 1	FSE-C	Prechlorination, tertiary (filtration) effluent	24-h composite	5/25/2004	46*	1833*			13	12	<0.50
System 1	CFE-Day1-C	Chlorinated final effluent	24-h composite	5/25/2004	420 / 410 (dup)	2,500			10	10	1
System 1	DS-Day1-G1	Distribution system, a.m.	Grab	5/25/2004	410	2,300	<0.1	2	13	13	1
System 1	DS-Day1-G2	Distribution system, p.m.	Grab	5/25/2004	330	2,400	<0.1	4			
System 1	CFE-Day2-C	Chlorinated final effluent	24-h composite	5/27/2004	520	2,500			10	10	1
System 1	DS-Day2-G1	Distribution system, a.m.	Grab	5/27/2004	400	2,200	<0.1	4	12	12	1
System 1	DS-Day2-G2	Distribution system, p.m.	Grab	5/27/2004	430	2,600	<0.1	4			
System 2	SE-C	Prechlorination, secondary effluent	24-h composite	9/29/2004	32*	389*	<0.1		--		2.044
System 2	FE1-C	Chlorinated final effluent	24-h composite	9/29/2004	97 / 96 (dup)	830 / 840 (dup)	<0.1	8.5	13.1	11.0	0.906
System 2	FE2-C	Chlorinated final effluent	24-h composite	9/29/2004	97	880	<0.1	8.3	13	11	0.981
System 2	P-G	Pond, chlorinated final effluent	Grab	9/29/2004	260	1,090	<0.1	6.4	12.8	11.7	0.442

* Samples were analyzed for NDMA and NDMA precursors at UC Berkeley.

Table C-3. Summary of Nonpotable Study Field Data

System 2	A1-G	Distribution system 1	Grab	9/29/2004	260	1,780	<0.1	5.8	12.4	11.2	0.404
System 2	DA1-G	Distribution system 2	Grab	9/29/2004	270	1,560	<0.1	4.2	10.7	9.52	0.114
System 2	RW-G	Post-irrigation recharge water	Grab	9/29/2004	ND	8.5	<0.1	0.1	6.7	6.9	0.455
System 3	FSE-C	Prechlorination, tertiary (filtration) effluent	24-h composite	5/3/2004	5	1,200	<0.1	<0.1	6.5	6.5	7.1
System 3	CCB-C	Chlorinated final effluent	24-h composite	5/3/2004	360	810	0.1	0.7	6.7	6.7	6.7
System 3	RWS-G1	Distribution system, a.m.	Grab	5/3/2004	120	730	<0.1	0.45	6.6	6.4	
System 3	RWS-G2	Distribution system, p.m.	Grab	5/3/2004	330 / 330 (dup)	780 / 770 (dup)	<0.1	0.9	6.7	6.6	
System 3	RWE-G1	Lake, a.m.	Grab	5/3/2004	3.9	170	<0.1	<0.1	9.6	5.8	
System 3	RWE-G2	Lake, p.m.	Grab	5/3/2004	10	460	<0.1	<0.1	5.5	5.4	
System 3	DMW 1-2	Monitoring well near recharge zone	Grab	7/13/2004	25	20			0.8	1.2	
System 3	DMW 4	Monitoring well near recharge zone	Grab	7/13/2004	5.4	11			1.3	0.9	
System 3	DMW 5	Monitoring well near recharge zone	Grab	7/13/2004	43	38			0.6	1.2	
System 3	SE-G	Prechlorination, secondary effluent	Grab	7/13/2004	27*	400*					0.22
System 3	FSE-C	Chlorinated final effluent	24-h composite	7/13/2004	140	620			6.0	6.1	0.05
System 3	FSE-G1	Chlorinated final effluent, p.m.	Grab	7/13/2004	57	760			6.1	5.6	0.04
System 3	CCB-G2	Chlorinated final effluent, a.m.	Grab	7/13/2004	250	850					

* Samples were analyzed for NDMA and NDMA precursors at UC Berkeley.

Table C-3. Summary of Nonpotable Study Field Data

System 3	RWS-C	Distribution system	24-h composite	7/13/2004	490	1,100			6	5.7	
System 3	RWE-G1	Lake, a.m.	Grab	7/13/2004	13	240	ND	0.7			
System 3	RWE-G2	Lake, p.m.	Grab	7/13/2004	2.5	210	ND	0.8			
System 3	DMW1-2	Monitoring well near recharge zone	Grab	7/13/2004	31	170					
System 3	DMW-5	Monitoring well near recharge zone	Grab	7/13/2004	27	21					
System 4	FSE-C	Prechlorination, tertiary (filtration) effluent	24-h composite	6/28/2004	100*	380*	<0.1	<0.1	7.82	7.08	0.044
System 4	CFE-C	Chlorinated final effluent	24-h composite	6/28/2004	260	630	<0.1	0.6	7.66	6.61	0.003
System 4	DS-C	Distribution system	24-h composite	6/28/2004	120	390	<0.1	0.7	7.74	6.71	<0.002
System 4	DS-G	Distribution system, p.m.	Grab	6/28/2004	82	330	<0.1	0.9	7.16	6.59	<0.002
System 5	SE	Prechlorination, secondary effluent	24-h composite	8/10/2004	9*	352*	<0.1	<0.1	6.5	5.4	0.061
System 5	FE	Chlorinated final effluent	24-h composite	8/10/2004	5.8	350					
System 5	DS1	Distribution system 1, a.m.	Grab	8/11/2004	7.8	86.0			6.1	5.9	
System 5	DS1	Distribution system 1, p.m.	Grab	8/11/2004	910	74.0					
System 5	DS2	Distribution system 2, a.m.	Grab	8/11/2004	6.0	67.0			6.1	6.0	
System 5	DS2	Distribution system 2, p.m.	Grab	8/11/2004	8.5	77.0					

* Samples were analyzed for NDMA and NDMA precursors at UC Berkeley.

Table C-3. Summary of Nonpotable Study Field Data

System 6	SCR	Distribution system 1, p.m.	Grab	5/10/2004	25	430	0.07	0.50	8.90	7.90	
System 6	VFPS	Pump station (distribution system 2), a.m.	Grab	5/10/2004	29 / 29 (dup)	170	0.23	0.63	8.10	8.60	
System 6	SCR	Distribution system 1, a.m.	Grab	5/10/2004	33	180	0.1	0.5	8.8	8.2	
System 6	VFPS	Pump station (distribution system 2), p.m.	Grab	5/10/2004	50	140	0.03	0.56	9.10	7.50	

* Samples were analyzed for NDMA and NDMA precursors at UC Berkeley.

Table C-3. Summary of Nonpotable Study Field Data

Utility	Sample ID	Sample Location	Sample Type	Sample Date	Nitrate/ Nitrite, mg/L	Nitrate, mg/L	Ammonia, mg/L	pH	Organic Nitrogen, mg/L	Total Kjeldahl Nitrogen, mg/L	Alkalinity (as CaCO3), mg/L
System 1	FSE-C	Prechlorination, tertiary (filtration) effluent	24-h composite	5/25/2004		<0.50	36				
System 1	CFE-Day1-C	Chlorinated final effluent	24-h composite	5/25/2004		<0.50	32				
System 1	DS-Day1-G1	Distribution system, a.m.	Grab	5/25/2004		<0.50	33				
System 1	DS-Day1-G2	Distribution system, p.m.	Grab	5/25/2004							
System 1	CFE-Day2-C	Chlorinated final effluent	24-h composite	5/27/2004		<0.50	30				
System 1	DS-Day2-G1	Distribution system, a.m.	Grab	5/27/2004		<0.50	30				
System 1	DS-Day2-G2	Distribution system, p.m.	Grab	5/27/2004							
System 2	SE-C	Prechlorination, secondary effluent	24-h composite	9/29/2004	2.14	0.1	34	8.1	0.4	34.4	327
System 2	FE1-C	Chlorinated final effluent	24-h composite	9/29/2004	2.25	1.34	28.5	8.1	0.6	29.2	298
System 2	FE2-C	Chlorinated final effluent	24-h composite	9/29/2004	2.32	1.34	31.5	8.1	0.8	32.3	299
System 2	P-G	Pond, chlorinated final effluent	Grab	9/29/2004	1.83	1.39	30.6	7.8	0.4	30.9	176

* Samples were analyzed for NDMA and NDMA precursors at UC Berkeley.

Table C-3. Summary of Nonpotable Study Field Data

Utility	Sample ID	Sample Location	Sample Type	Sample Date	Nitrate/ Nitrite, mg/L	Nitrate, mg/L	Ammonia, mg/L	pH	Organic Nitrogen, mg/L	Total Kjeldahl Nitrogen, mg/L	Alkalinity (as CaCO3), mg/L
System 2	A1-G	Distribution system 1	Grab	9/29/2004	1.84	1.44	26.5	7.9	0.4	26.9	266
System 2	DA1-G	Distribution system 2	Grab	9/29/2004	98.9	98.8	0.2	8.1	<0.1	<0.2	433
System 2	RW-G	Post-irrigation recharge water	Grab	9/29/2004	2.03	1.57	30.6	7.8	0.4	31	283
System 3	FSE-C	Prechlorination, tertiary (filtration) effluent	24-h composite	5/3/2004		0.045	0.13				
System 3	CCB-C	Chlorinated final effluent	24-h composite	5/3/2004		0.016	0.26				
System 3	RWS-G1	Distribution system, a.m.	Grab	5/3/2004							
System 3	RWS-G2	Distribution system, p.m.	Grab	5/3/2004							
System 3	RWE-G1	Lake, a.m.	Grab	5/3/2004							
System 3	RWE-G2	Lake, p.m.	Grab	5/3/2004							
System 3	DMW 1-2	Monitoring well near recharge zone	Grab	7/13/2004							
System 3	DMW 4	Monitoring well near recharge zone	Grab	7/13/2004							
System 3	DMW 5	Monitoring well near recharge zone	Grab	7/13/2004							
System 3	SE-G	Prechlorination, secondary effluent	Grab	7/13/2004		11.1	0.47				
System 3	FSE-C	Chlorinated final effluent	24-h	7/13/2004		10.6	0.1				

* Samples were analyzed for NDMA and NDMA precursors at UC Berkeley.

Table C-3. Summary of Nonpotable Study Field Data

Utility	Sample ID	Sample Location	Sample Type	Sample Date	Nitrate/ Nitrite, mg/L	Nitrate, mg/L	Ammonia, mg/L	pH	Organic Nitrogen, mg/L	Total Kjeldahl Nitrogen, mg/L	Alkalinity (as CaCO3), mg/L
			composite								
System 3	FSE-G1	Chlorinated final effluent, p.m.	Grab	7/13/2004		8.2	0.65				
System 3	CCB-G2	Chlorinated final effluent, a.m.	Grab	7/13/2004							
System 3	RWS-C	Distribution system	24-h composite	7/13/2004							
System 3	RWE-G1	Lake, a.m.	Grab	7/13/2004							
System 3	RWE-G2	Lake, p.m.	Grab	7/13/2004							
System 3	DMW1-2	Monitoring well near recharge zone	Grab	7/13/2004							
System 3	DMW-5	Monitoring well near recharge zone	Grab	7/13/2004							
System 4	FSE-C	Prechlorination, tertiary (filtration) effluent	24-h composite	6/28/2004	20.8	20.8	<0.1	7.5	0.6	0.6	101
System 4	CFE-C	Chlorinated final effluent	24-h composite	6/28/2004	18.9	18.9	<0.1	7.5	0.9	0.9	93.5
System 4	DS-C	Distribution system	24-h composite	6/28/2004	19.0	19.0	<0.1	7.6	0.8	0.8	88.6
System 4	DS-G	Distribution system, p.m.	Grab	6/28/2004	18.7	18.7	<0.1	7.5	0.6	0.6	88.4

* Samples were analyzed for NDMA and NDMA precursors at UC Berkeley.

Table C-3. Summary of Nonpotable Study Field Data

Utility	Sample ID	Sample Location	Sample Type	Sample Date	Nitrate/ Nitrite, mg/L	Nitrate, mg/L	Ammonia, mg/L	pH	Organic Nitrogen, mg/L	Total Kjeldahl Nitrogen, mg/L	Alkalinity (as CaCO3), mg/L
System 5	SE	Prechlorination, secondary effluent	24-h composite	8/10/2004	5.36	5.3	<0.1	7.7	0.7	0.7	149
System 5	FE	Chlorinated final effluent	24-h composite	8/10/2004							
System 5	DS1	Distribution system 1, a.m.	Grab	8/11/2004							
System 5	DS1	Distribution system 1, p.m.	Grab	8/11/2004							
System 5	DS2	Distribution system 2, a.m.	Grab	8/11/2004							
System 5	DS2	Distribution system 2, p.m.	Grab	8/11/2004							
System 6	SCR	Distribution system 1, p.m.	Grab	5/10/2004							
System 6	VFPS	Pump station (distribution system 2), a.m.	Grab	5/10/2004							
System 6	SCR	Distribution system 1, a.m.	Grab	5/10/2004							
System 6	VFPS	Pump station (distribution system 2), p.m.	Grab	5/10/2004							

* Samples were analyzed for NDMA and NDMA precursors at UC Berkeley.

Table C-4. Summary of Nonpotable Study Laboratory Data

		NDMA conc, ng/L (mean ± SD) at:				
Facility	**Chlorine conc, mg Cl2/L**	**0 h**	**1 h**	**10 h**	**50 h**	**50 h (sterile)**
System 1	0	46 ± 2			56 ± 3	63 ± 2
	2.5		38 ± 2	50 ± 2	116 ± 5	
	5		40 ± 2	237 ± 9	996 ± 60	
	10		39 ± 2	854 ± 57	1833 ± 88	
System 2	0	32 ± 8			27 ± 14	17 ± 8
	2.5		20 ± 8	19 ± 8	14 ± 8	
	5		27 ± 8	16 ± 8	16 ± 16	
	10		78 ± 16	21 ± 4	19 ± 2	
System 3	0	27 ± 19			42 ± 40	23 ± 16
	2.5		32± 14	96 ±16	85 ± 13	
	5		30± 24	24± 13	19 ± 4	
	10		55 ± 32	27 ±15	39 ± 8	
System 4	0	120 ±13; 81±31			78 ± 16	88 ± 16
	2.5		86 ± 10	76 ± 16	77 ± 16	
	5		76 ± 16	39 ± 14	20 ± 1	
	10		78 ± 16	21 ± 4	19 ± 2	
System 5	0	9 ± 1			6 ± 1	9 ± 4
	2.5		9 ± 4	14 ± 3	15 ± 3	
	5		7 ± 2	8 ± 2	18 ± 4	
	10		6 ± 2	7 ± 1	10 ± 2	
	2.5*		5 ± 1	6 ± 1	20 ± 1	
	5*		8 ± 1	15 ± 1	127 ± 1	
	10*		8 ± 1	97 ± 5	296 ± 1	

APPENDIX D

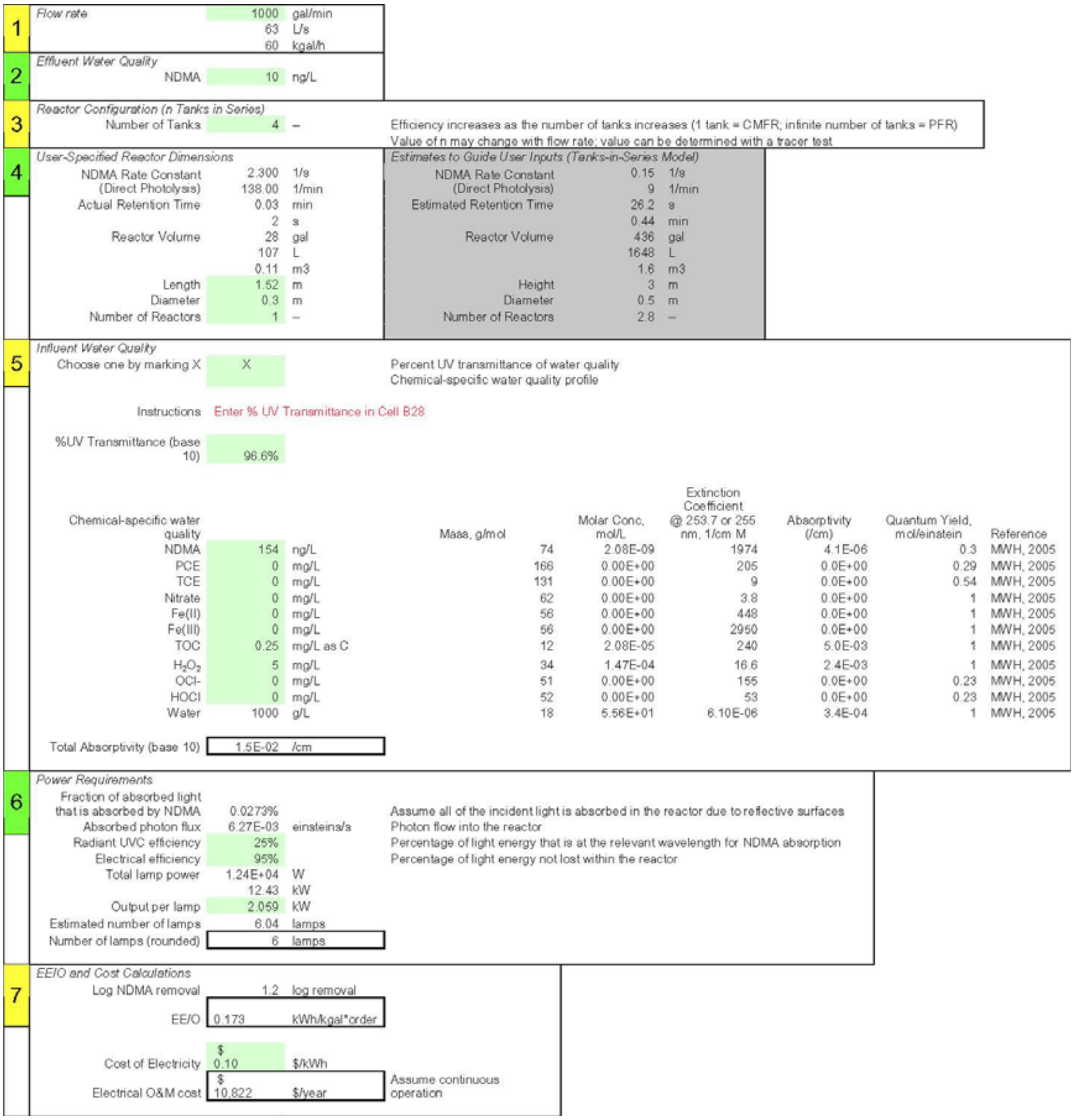
UV PHOTOLYSIS MODEL

D.1 SUMMARY

The UV photolysis model spreadsheets included in this Appendix were developed to help utilities predict UV treatment performance and costs for different flow rates, influent water quality, UV reactor size, hydraulic configuration, and lamp power. The UV reactor was modeled as the equivalent of *n* completely mixed tanks in series. Model equations are explained in Chapter 6.

Some of the spreadsheet cells in the model are shaded; values for these parameters should be entered by the user. All other values are calculated by the model. Key model results are emphasized by a border. To increase the model's flexibility, several versions of the model were developed. The first version (Table D-1) allows the user to predict power requirements to meet a target effluent NDMA concentration. The second version (Table D-2) allows the user to predict NDMA effluent concentrations for a given reactor with a fixed lamp power. The third version of the model (Table D-3) allows the user to predict the best-fit value of *n* (number of tanks in series) to characterize the reactor hydraulic configuration. More details on each of these models is contained in Chapter 6.

Table D-1. UV Photolysis Model to Predict Power Requirements and Electricity Costs



1 *Flow rate*

Flow rate	1000	gal/min
	63	L/s
	60	kgal/h

2 *Effluent Water Quality*

NDMA	10	ng/L

3 *Reactor Configuration (n Tanks in Series)*

Number of Tanks	4	–	Efficiency increases as the number of tanks increases (1 tank = CMFR; infinite number of tanks = PFR) Value of n may change with flow rate; value can be determined with a tracer test

4 *User-Specified Reactor Dimensions* / *Estimates to Guide User Inputs (Tanks-in-Series Model)*

User-Specified Reactor Dimensions			*Estimates to Guide User Inputs (Tanks-in-Series Model)*		
NDMA Rate Constant	2.300	1/s	NDMA Rate Constant	0.15	1/s
(Direct Photolysis)	138.00	1/min	(Direct Photolysis)	9	1/min
Actual Retention Time	0.03	min	Estimated Retention Time	26.2	s
	2	s		0.44	min
Reactor Volume	28	gal	Reactor Volume	436	gal
	107	L		1648	L
	0.11	m3		1.6	m3
Length	1.52	m	Height	3	m
Diameter	0.3	m	Diameter	0.5	m
Number of Reactors	1	–	Number of Reactors	2.8	–

5 *Influent Water Quality*

Choose one by marking X	X	Percent UV transmittance of water quality
		Chemical-specific water quality profile

Instructions Enter % UV Transmittance in Cell B28

%UV Transmittance (base 10) 96.6%

Chemical-specific water quality			Mass, g/mol	Molar Conc, mol/L	Extinction Coefficient @ 253.7 or 255 nm, 1/cm M	Absorptivity (/cm)	Quantum Yield, mol/einstein	Reference
NDMA	154	ng/L	74	2.08E-09	1974	4.1E-06	0.3	MWH, 2005
PCE	0	mg/L	166	0.00E+00	205	0.0E+00	0.29	MWH, 2005
TCE	0	mg/L	131	0.00E+00	9	0.0E+00	0.54	MWH, 2005
Nitrate	0	mg/L	62	0.00E+00	3.8	0.0E+00	1	MWH, 2005
Fe(II)	0	mg/L	56	0.00E+00	448	0.0E+00	1	MWH, 2005
Fe(III)	0	mg/L	56	0.00E+00	2950	0.0E+00	1	MWH, 2005
TOC	0.25	mg/L as C	12	2.08E-05	240	5.0E-03	1	MWH, 2005
H_2O_2	5	mg/L	34	1.47E-04	16.6	2.4E-03	1	MWH, 2005
OCl-	0	mg/L	51	0.00E+00	155	0.0E+00	0.23	MWH, 2005
HOCl	0	mg/L	52	0.00E+00	53	0.0E+00	0.23	MWH, 2005
Water	1000	g/L	18	5.56E+01	6.10E-06	3.4E-04	1	MWH, 2005

Total Absorptivity (base 10) 1.5E-02 /cm

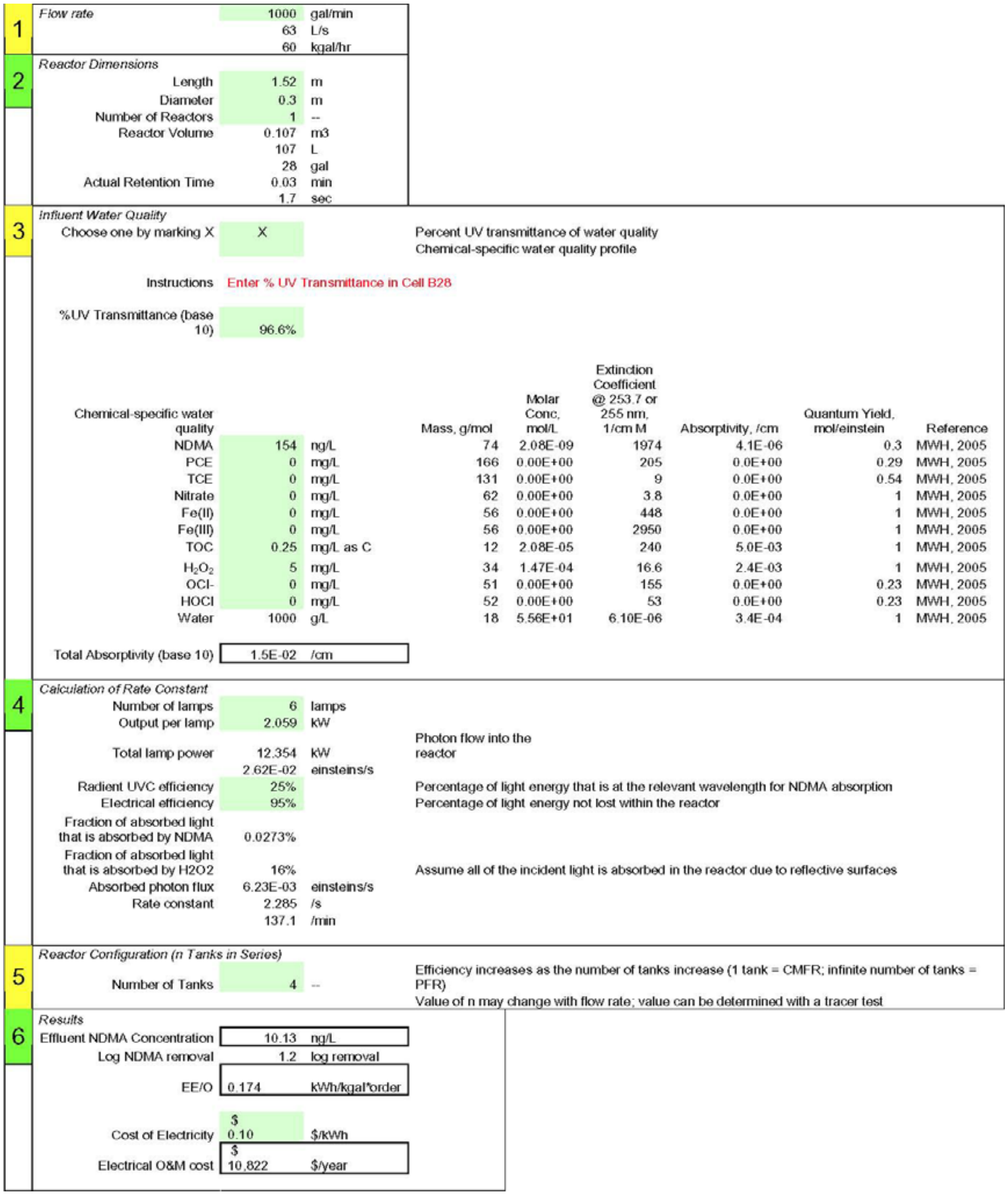
6 *Power Requirements*

Fraction of absorbed light that is absorbed by NDMA	0.0273%		Assume all of the incident light is absorbed in the reactor due to reflective surfaces
Absorbed photon flux	6.27E-03	einsteins/s	Photon flow into the reactor
Radiant UVC efficiency	25%		Percentage of light energy that is at the relevant wavelength for NDMA absorption
Electrical efficiency	95%		Percentage of light energy not lost within the reactor
Total lamp power	1.24E+04	W	
	12.43	kW	
Output per lamp	2.059	kW	
Estimated number of lamps	6.04	lamps	
Number of lamps (rounded)	6	lamps	

7 *EE/O and Cost Calculations*

Log NDMA removal	1.2	log removal	
EE/O	0.173	kWh/kgal*order	
Cost of Electricity	$ 0.10	$/kWh	
Electrical O&M cost	$ 10,822	$/year	Assume continuous operation

Table D-2. Photolysis Model to Predict NDMA Effluent Concentration

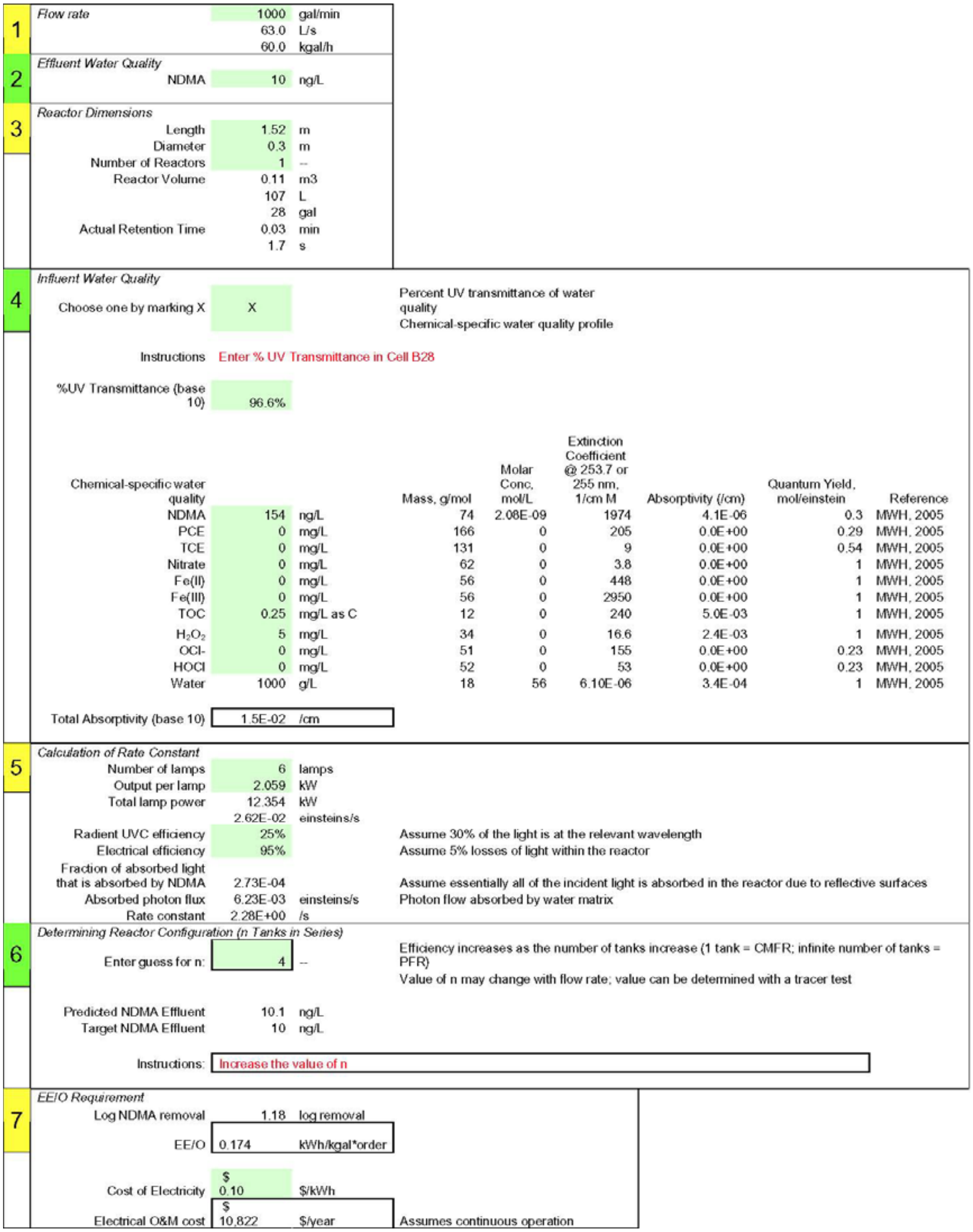


1	*Flow rate*	1000	gal/min	
		63	L/s	
		60	kgal/hr	
2	*Reactor Dimensions*			
	Length	1.52	m	
	Diameter	0.3	m	
	Number of Reactors	1	--	
	Reactor Volume	0.107	m3	
		107	L	
		28	gal	
	Actual Retention Time	0.03	min	
		1.7	sec	
3	*Influent Water Quality*			
	Choose one by marking X	X		Percent UV transmittance of water quality
				Chemical-specific water quality profile
	Instructions	Enter % UV Transmittance in Cell B28		
	%UV Transmittance (base 10)	96.6%		

Chemical-specific water quality			Mass, g/mol	Molar Conc, mol/L	Extinction Coefficient @ 253.7 or 255 nm, 1/cm M	Absorptivity, /cm	Quantum Yield, mol/einstein	Reference
NDMA	154	ng/L	74	2.08E-09	1974	4.1E-06	0.3	MWH, 2005
PCE	0	mg/L	166	0.00E+00	205	0.0E+00	0.29	MWH, 2005
TCE	0	mg/L	131	0.00E+00	9	0.0E+00	0.54	MWH, 2005
Nitrate	0	mg/L	62	0.00E+00	3.8	0.0E+00	1	MWH, 2005
Fe(II)	0	mg/L	56	0.00E+00	448	0.0E+00	1	MWH, 2005
Fe(III)	0	mg/L	56	0.00E+00	2950	0.0E+00	1	MWH, 2005
TOC	0.25	mg/L as C	12	2.08E-05	240	5.0E-03	1	MWH, 2005
H_2O_2	5	mg/L	34	1.47E-04	16.6	2.4E-03	1	MWH, 2005
OCl-	0	mg/L	51	0.00E+00	155	0.0E+00	0.23	MWH, 2005
HOCl	0	mg/L	52	0.00E+00	53	0.0E+00	0.23	MWH, 2005
Water	1000	g/L	18	5.56E+01	6.10E-06	3.4E-04	1	MWH, 2005

	Total Absorptivity (base 10)	1.5E-02	/cm	
4	*Calculation of Rate Constant*			
	Number of lamps	6	lamps	
	Output per lamp	2.059	kW	
	Total lamp power	12.354	kW	Photon flow into the reactor
		2.62E-02	einsteins/s	
	Radient UVC efficiency	25%		Percentage of light energy that is at the relevant wavelength for NDMA absorption
	Electrical efficiency	95%		Percentage of light energy not lost within the reactor
	Fraction of absorbed light that is absorbed by NDMA	0.0273%		
	Fraction of absorbed light that is absorbed by H2O2	16%		Assume all of the incident light is absorbed in the reactor due to reflective surfaces
	Absorbed photon flux	6.23E-03	einsteins/s	
	Rate constant	2.285	/s	
		137.1	/min	
5	*Reactor Configuration (n Tanks in Series)*			
	Number of Tanks	4	--	Efficiency increases as the number of tanks increase (1 tank = CMFR; infinite number of tanks = PFR) Value of n may change with flow rate; value can be determined with a tracer test
6	*Results*			
	Effluent NDMA Concentration	10.13	ng/L	
	Log NDMA removal	1.2	log removal	
	EE/O	0.174	kWh/kgal*order	
	Cost of Electricity	$ 0.10	$/kWh	
	Electrical O&M cost	$ 10,822	$/year	

Table D-3. UV Photolysis Model to Predict Best-Fit Hydraulic Reactor Configuration



1	*Flow rate*	1000	gal/min
		63.0	L/s
		60.0	kgal/h
2	*Effluent Water Quality*		
	NDMA	10	ng/L
3	*Reactor Dimensions*		
	Length	1.52	m
	Diameter	0.3	m
	Number of Reactors	1	--
	Reactor Volume	0.11	m3
		107	L
		28	gal
	Actual Retention Time	0.03	min
		1.7	s

4	*Influent Water Quality*		
	Choose one by marking X		Percent UV transmittance of water quality
		X	Chemical-specific water quality profile
	Instructions	Enter % UV Transmittance in Cell B28	
	%UV Transmittance (base 10)	96.6%	

Chemical-specific water quality			Mass, g/mol	Molar Conc, mol/L	Extinction Coefficient @ 253.7 or 255 nm, 1/cm M	Absorptivity (/cm)	Quantum Yield, mol/einstein	Reference
NDMA	154	ng/L	74	2.08E-09	1974	4.1E-06	0.3	MWH, 2005
PCE	0	mg/L	166	0	205	0.0E+00	0.29	MWH, 2005
TCE	0	mg/L	131	0	9	0.0E+00	0.54	MWH, 2005
Nitrate	0	mg/L	62	0	3.8	0.0E+00	1	MWH, 2005
Fe(II)	0	mg/L	56	0	448	0.0E+00	1	MWH, 2005
Fe(III)	0	mg/L	56	0	2950	0.0E+00	1	MWH, 2005
TOC	0.25	mg/L as C	12	0	240	5.0E-03	1	MWH, 2005
H_2O_2	5	mg/L	34	0	16.6	2.4E-03	1	MWH, 2005
OCl-	0	mg/L	51	0	155	0.0E+00	0.23	MWH, 2005
HOCl	0	mg/L	52	0	53	0.0E+00	0.23	MWH, 2005
Water	1000	g/L	18	56	6.10E-06	3.4E-04	1	MWH, 2005
Total Absorptivity (base 10)	1.5E-02	/cm						

5	*Calculation of Rate Constant*			
	Number of lamps	6	lamps	
	Output per lamp	2.059	kW	
	Total lamp power	12.354	kW	
		2.62E-02	einsteins/s	
	Radient UVC efficiency	25%		Assume 30% of the light is at the relevant wavelength
	Electrical efficiency	95%		Assume 5% losses of light within the reactor
	Fraction of absorbed light that is absorbed by NDMA	2.73E-04		Assume essentially all of the incident light is absorbed in the reactor due to reflective surfaces
	Absorbed photon flux	6.23E-03	einsteins/s	Photon flow absorbed by water matrix
	Rate constant	2.28E+00	/s	
6	*Determining Reactor Configuration (n Tanks in Series)*			
	Enter guess for n:	4	--	Efficiency increases as the number of tanks increase (1 tank = CMFR; infinite number of tanks = PFR) Value of n may change with flow rate; value can be determined with a tracer test
	Predicted NDMA Effluent	10.1	ng/L	
	Target NDMA Effluent	10	ng/L	
	Instructions:	Increase the value of n		
7	*EE/O Requirement*			
	Log NDMA removal	1.18	log removal	
	EE/O	0.174	kWh/kgal*order	
	Cost of Electricity	$ 0.10	$/kWh	
	Electrical O&M cost	$ 10,822	$/year	Assumes continuous operation

Advancing the Science of Water Reuse and Desalination

WATEREUSE
FOUNDATION

1199 North Fairfax Street, Suite 410
Alexandria, VA 22314 USA
(703) 548-0880
Fax (703) 548-5085
E-mail: Foundation@WateReuse.org
www.WateReuse.org/Foundation