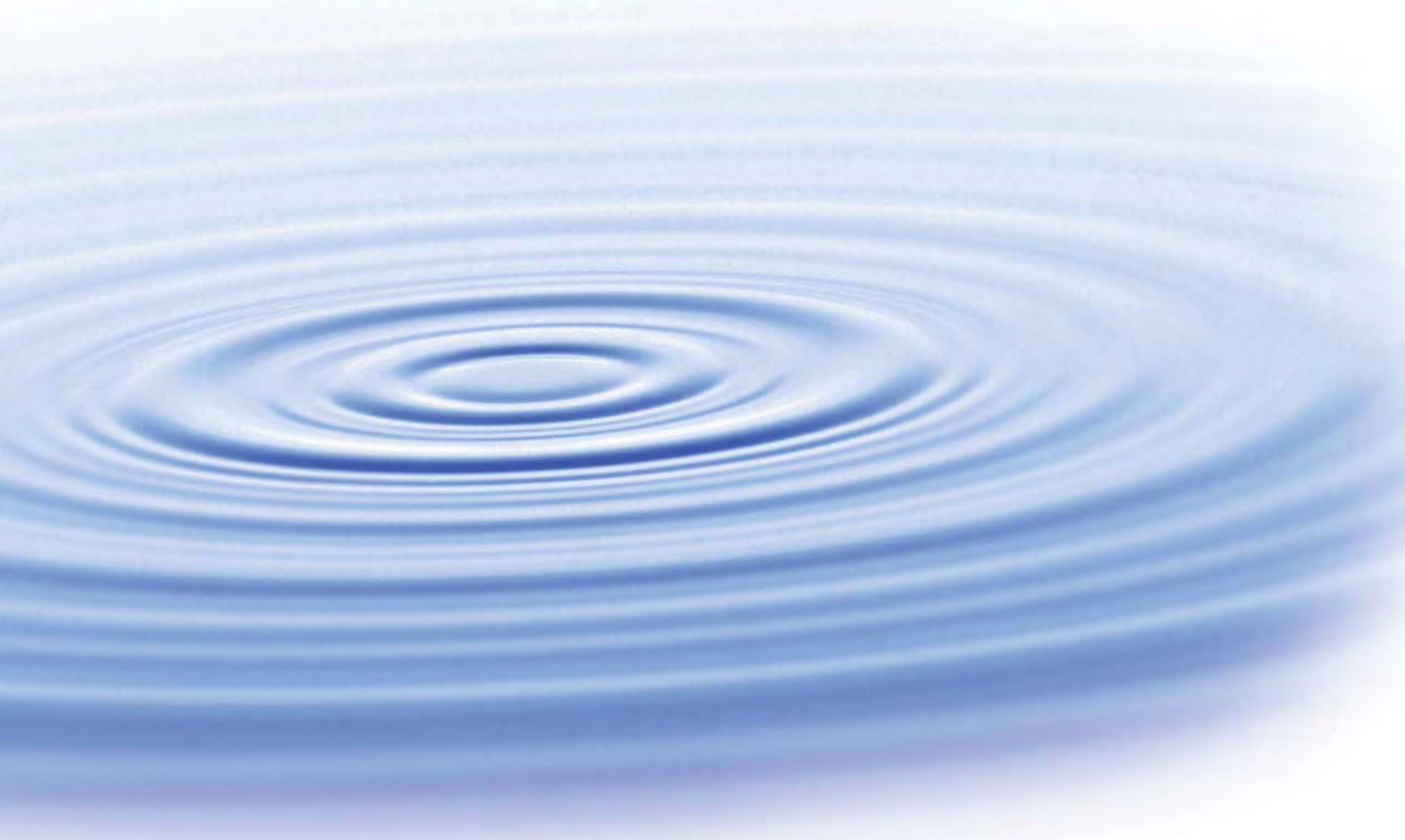
WATEREUSE
FOUNDATION

# Investigation of *N*-itrosodimethylamine (NDMA) Fate and Transport



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## 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.

# Investigation of *N*-Nitrosodimethylamine (NDMA) Fate and Transport

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# 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 study sponsored by the Foundation and is intended to communicate the results of this research project. The overall objective of the project is to assess the fate and transport of NDMA and NDMA precursors in soil, groundwater, and surface waters. The project includes a review of available data from NDMA contaminated sites to identify environmental variables that influence NDMA transport and transformation. The project also includes experimental studies to assess the potential for biotransformation and field studies to assess volatilization and transport of NDMA in irrigated soil plots and soil columns.

| | |
|---|---|
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# EXECUTIVE SUMMARY

*N*-Nitrosodimethylamine (NDMA) is a polar, uncharged organic compound that is frequently present in wastewater effluent. In response to human health concerns associated with NDMA, water utilities and regulatory agencies have dedicated substantial effort to monitoring NDMA and attempting to reduce NDMA concentrations in wastewater effluent. While source control and modifications of treatment processes may lead to decreases in NDMA concentrations in wastewater, it is extremely difficult to achieve the stringent levels derived for protection of public health without installing expensive, advanced treatment systems. Therefore, NDMA in wastewater effluent could enter potable water supplies when wastewater effluent is used for landscape irrigation or groundwater recharge. To assess the potential for NDMA in wastewater effluent to enter potable water supplies through these mechanisms, a research project was conducted between 2002 and 2005 by a team of researchers from University of California (UC) Berkeley, UC Riverside, Arizona State University, and Todd Engineers. The research team reviewed existing data on NDMA fate and transport and conducted laboratory experiments to determine the fate of NDMA and NDMA precursors under the conditions encountered in landscape irrigation and groundwater recharge systems.

A review of field data from five different sites where NDMA was released to groundwater indicated that NDMA is persistent and highly mobile in groundwater. At two of the sites, the NDMA originated in wastes from rocket testing and manufacturing, while at the remaining sites, NDMA originated from infiltration or injection of wastewater effluent. Examination of hydrogeologic studies and field data indicated that sorption does not significantly retard the transport of NDMA in groundwater. Analysis of NDMA degradation in groundwater was limited by the lack of sensitive NDMA analytical methods prior to 2000. Degradation of NDMA was inferred at one of the five sites based on monitoring data and hydrogeologic information. If NDMA degradation occurred at the remaining sites, it was not possible to detect the losses from the available monitoring data.

Previously published studies indicated that NDMA undergoes biodegradation under certain conditions. To gain further insight into the importance of biotransformation of NDMA in soil and groundwater under conditions encountered in water reuse systems, laboratory experiments were conducted with pure cultures of bacteria that express monooxygenase enzymes and mixed cultures derived from soils. Results from these studies indicated that NDMA undergoes biodegradation on the time scale of hours to days in the presence of oxygen and labile organic matter that can serve as a carbon source for the bacteria. Therefore, NDMA should undergo biodegradation as it passes through surface soils. Similar experiments, conducted to assess the stability of NDMA precursors, indicated that the precursors present in wastewater effluent were relatively stable, with decreases in concentration of less than 30% over periods up to 30 days.

To assess the fate of NDMA in landscape irrigation systems, experiments were conducted by applying NDMA-containing wastewater effluent to turfgrass plots equipped with suction lysimeters for sampling water that passed through the vadose zone. Results of these experiments indicated that nearly all of the NDMA was removed as water passed through the unsaturated zone through processes including volatilization and biodegradation.

Complementary experiments with intact soil cores suggested that the loss of NDMA was mainly attributable to volatilization.

To assess the fate of NDMA and NDMA precursors derived from wastewater effluent in groundwater, NDMA-containing wastewater effluent was applied to a saturated column with a hydraulic retention time of approximately 20 days. The concentration of both NDMA and NDMA precursors in the column effluent was less than 25% of the column influent concentrations. In contrast, saturated columns that received surface water amended with NDMA showed little or no removal of NDMA under similar flow conditions. The enhanced removal of NDMA in the columns fed with wastewater effluent appears to have been related to the presence of labile organic carbon in the wastewater effluent.

Results from this study indicate that NDMA and NDMA precursors in wastewater effluent may be removed during landscape irrigation or groundwater recharge under certain conditions. In landscape irrigation systems, NDMA can volatilize from soil pore water within the first few hours of application. NDMA may also undergo biodegradation in the vadose zone if the retention time is sufficient and if the appropriate microbial community is present. In soil aquifer treatment systems where NDMA in secondary or tertiary wastewater effluent percolates through soil, partial NDMA degradation may occur as the labile organic carbon is metabolized. NDMA precursors also are removed during passage through saturated soils, presumably through a combination of sorption and biotransformation. In groundwater recharge systems where water is subjected to advanced treatment prior to direct injection into groundwater, the potential for biodegradation is lower because labile organic carbon is removed during the treatment process. However, partial degradation of NDMA was inferred from field data collected at a site where water was subjected to reverse osmosis prior to injection. Additional research is needed to assess the potential for NDMA degradation in this system and other systems with similar characteristics.

# CHAPTER 1

# INTRODUCTION

*N*-Nitrosodimethylamine (NDMA) is a polar, uncharged organic compound that was detected in California in 1998 during an investigation of groundwater contamination near industrial facilities where liquid rocket fuel was used. As part of the California Department of Health Services (CDHS) investigation of groundwater contamination, a sensitive analytical method was used to measure NDMA in background samples at locations far from industrial sources of the compound. Results of the CDHS study and follow-up investigations conducted by utilities indicate that NDMA is present in recycled water from municipal wastewater treatment plants (WWTPs) and advanced treatment plants at concentrations above the current Notification Level (NL) of 10 ng/L.[1]

Although NDMA is listed as a priority pollutant, a maximum contaminant level has not been established. On the basis of cancer potency data reviewed by the U.S. Environmental Protection Agency (USEPA) (Liteplo et al., 2002), the USEPA established a cleanup level of 0.7 ng/L for NDMA in groundwater at a rocket-testing facility located near Sacramento, California (*Record of Decision*, 2001). As a result of these stringent guidelines, water-recycling programs are being scrutinized for their potential to introduce NDMA into groundwater. In 2001, the WateReuse Foundation (WRF) responded to these concerns by funding a study of methods for determining occurrence and minimizing the concentrations of NDMA produced by advanced WWTPs. However, results of this research are unlikely to eliminate all of the NDMA from recycled water. Furthermore, indirect potable reuse programs and nonpotable water reuse programs sometimes use chlorinated secondary wastewater effluent that often contains concentrations of NDMA over the CDHS's response level (RL) of 200 ng/L (Sedlak et al., 2005). With the detection of NDMA in final effluents, it has been suggested that the use of recycled water for landscape irrigation could contaminate drinking-water aquifers.[2]

To understand the potential impact of NDMA from recycled water, research is needed to assess the fate of NDMA when effluent from conventional and advanced WWTPs is used for landscape irrigation applied by spray irrigation and aquifer recharge by surface spreading and direct injection. While there are many other forms of recycled-water irrigation (e.g., drip, flood, pivot.), this project focuses on spray irrigation, which is one of the most common systems used for landscape irrigation. When NDMA-containing wastewater effluent is used

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[1] The State of California has established an NL for NDMA of 10 ng/L or parts per trillion (ppt). NLs are health-based advisory levels established by CDHS for chemicals in drinking water that lack maximum contaminant levels (MCLs). An NL is the level of a contaminant in drinking water that is considered not to pose a significant health risk to people ingesting that water on a daily basis. There are public notification requirements for drinking-water systems when a contaminant in excess of an NL or an MCL is discovered in a drinking-water well, or when the well is closed due to the contaminant's presence. The CDHS has also set a response level (RL) for NDMA of 200 ng/L. CDHS recommends that the drinking-water system be taken out of service if NDMA concentration in the well or water supply exceeds the RL.

[2] A lawsuit was filed against the City of San Jose, California. The South Bay Recycled Water Program called for an expansion of a tertiary treated recycled-water pipeline that would serve a local power plant and provide water for irrigation projects en route. Parties who filed the lawsuit have claimed that the recycled water contains harmful levels of NDMA and, if used for irrigation, would contaminate groundwater and pose a risk to public health and safety as well as the environment.

for landscape irrigation, it is anticipated that some NDMA removal will occur in the vadose zone or under saturated flow conditions (i.e., in groundwater) by biodegradation. In many cases, the biodegradation will be coupled with sorption of NDMA to soil or aquifer solids, which will slow the transport of NDMA. Although the sorption and biotransformation of NDMA have been studied in several previous research projects, the rates and mechanisms of these processes have not been studied under conditions that are relevant to water reuse.

In addition to NDMA, municipal wastewater effluent also contains high concentrations of NDMA precursors relative to other water sources (Mitch et al., 2003a; Mitch and Sedlak, 2004). The exact identity of the NDMA precursors is unknown, but it has been shown that the NDMA precursors in wastewater effluent can be converted into NDMA during disinfection in water treatment plants or drinking-water distribution systems. At present, little is known about the environmental fate of NDMA precursors in soil and groundwater. To assess the potential for wastewater-derived NDMA precursors to enter water supplies, research is needed on the fate and transport of NDMA precursors.

# CHAPTER 2

# NDMA OCCURRENCE, FATE, AND TRANSPORT IN GROUNDWATER

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Todd Engineers evaluated the fate and transport of NDMA in groundwater through the documentation of hydrogeologic and water quality conditions at six locations where NDMA releases to groundwater have occurred. This evaluation and documentation provide the context for interpreting the laboratory and experimental components of the research project.

## 2.1 SCOPE AND METHODOLOGY

The evaluation and documentation examined conditions at sites where NDMA had been released to groundwater through a variety of release mechanisms. At these sites, a source water containing NDMA (i.e., industrial wastewater or recycled water) was either intentionally or unintentionally released to the environment and eventually reached underlying groundwater. Unintentional releases include industrial spills, leaks, or land disposal of wastewater containing dissolved NDMA. Intentional releases include surface recharge or injection of recycled water containing NDMA for specific purposes such as groundwater replenishment or the hydraulic control of seawater intrusion.

The study relied on existing data that typically included the following data sets:

- Water quality data (including NDMA analysis) for source water and groundwater
- Operational data on the extent and nature of the release
- Aquifer delineation and aquifer parameters
- Groundwater flow system information

The persistence of NDMA in downgradient groundwater was examined using NDMA sampling results of monitoring and production wells. Where data were sufficiently complete, maps were prepared showing concentrations of NDMA in downgradient groundwater (plume maps). Plume maps were especially helpful at the sites where NDMA has been in groundwater for decades.

Plume mapping at any site where contaminants have been released into the groundwater system generally shows decreasing concentrations of the contaminant with distance from the release site. These decreasing concentrations downgradient can result from a number of factors. For this study, the following conditions were considered as possible explanations of decreasing NDMA concentrations in downgradient groundwater wells:

- Well location or construction prevents the intersection of the well screen and impacted groundwater;
- Well is sampling a combination of NDMA-impacted groundwater and nonimpacted groundwater (mixing in the well);
- NDMA has been impeded through the process of sorption onto sediment particles, slowing the migration of NDMA with respect to groundwater velocity and temporarily removing mass from the groundwater system;

- NDMA has dispersed (spread out) in the aquifer, lowering concentrations and increasing the area of impact;
- NDMA has been mixed with native groundwater by induced vertical or lateral gradients from pumping wells;
- NDMA has been transformed by biodegradation, chemical reaction, or another process that has decreased the mass of NDMA in the system.

In order to differentiate among these mechanisms, site-specific groundwater conditions and well data were examined. At some sites, constituents other than NDMA were used to identify the movement of the source water. If source water was being diluted or mixed in a well, then the dissolved NDMA was also being diluted. If the release occurred in only part of the aquifer, source water could disperse throughout the aquifer, lowering concentrations of NDMA. If data indicated that a well sample contained a large percentage of source water with NDMA concentrations significantly lower than in source water at the release point, then mass removal was inferred.

This methodology was difficult to apply if complete source water data were unavailable or if the chemical composition of the source water was too similar to that of groundwater. It was determined separately that sorption was not an important process in the attenuation of NDMA, given specific chemical properties as discussed in more detail in the following sections.

## 2.2 SITES SELECTED FOR ANALYSIS

Six sites were selected for analysis that covered a wide variety of site conditions in terms of type of release, source water concentrations, and hydrogeologic/geochemical conditions. Criteria for site selection included the following:

- Release of NDMA to groundwater
- Variety of sources of release (aerospace/industrial and recycled-water projects)
- Water quality data for source water and groundwater
- Variety of release mechanisms (e.g., spills, recharge basins, injection wells, and irrigation)
- Variety of hydrogeologic conditions
- Different ages of NDMA releases (i.e., >20 years ago and more recent releases)
- Ready availability of public data

After use of these criteria, the following six sites were selected for analysis. Sites are listed from oldest release to most recent release.

**Table 2.1. Selected Sites for NDMA Analysis**[1]

| Site | NDMA release |  | Groundwater basin | Data source |
|---|---|---|---|---|
|  | Source | Type |  |  |
| San Gabriel Valley BPOU | Industrial | Spills, disposal | San Gabriel | USEPA |
| Rancho Cordova Aerospace Facility | Industrial | Spills, disposal | Sacramento Valley | CVRWQCB |
| MFRP | Recycled water | Recharge basins | Central Basin | LACSD |
| Talbert Barrier Injection Project | Recycled water | Injection wells | Orange Co. coastal plain | OCWD |
| West Coast Barrier Injection Project | Recycled water | Injection wells | West Coast Basin | WBMWD |
| South Bay Water Recycling Project | Recycled water | Irrigation | Santa Clara Valley | SCVWD |

[1] BPOU, Baldwin Park Operable Unit of the San Gabriel Basin Superfund Sites;
USEPA, USEPA, Region IX;
CVRWQCB, Regional Water Quality Control Board, Central Valley Region;
MFRP, Montebello Forebay Recharge Project;
LACSD, Sanitation Districts of Los Angeles County;
OCWD, Orange County Water District;
WBMWD, West Basin Municipal Water District;
SCVWD, Santa Clara Valley Water District.

Four of the sites are in Southern California, and two are in Northern California, as shown in Figure 2.1. The four sites in Southern California are located on the coastal plain of Los Angeles and Orange counties and nearby inland basins, as shown in Figure 2.2. All of the groundwater basins contain unconsolidated alluvial sediments dating from recent times to the Pliocene Age. Aquifers represent a variety of depositional environments, including continental fluvial deposits, alluvial fans, and coastal marine sands.

Each type of site provides certain benefits in terms of relevant data. For the industrial sites, more detailed monitoring data were generally available, but source waters were not well characterized. Higher NDMA concentrations in groundwater at the industrial sites enhanced the ability to track concentrations further downgradient. For the recycled-water sites, more detailed data on operation, timing of release, and source water concentrations were available. The South Bay Water Recycling Project did not have sufficient groundwater data to make a fate and transport assessment (e.g., no NDMA sampling) and is included to summarize data to date and make recommendations for additional data collection.

**Figure 2.1. Selected Sites for NDMA Analysis.**

In terms of timing of release, four of the six sites released NDMA to groundwater more than 20 years ago, allowing for a more detailed assessment of fate and transport. Where NDMA had been recently released, impacts to groundwater involved fewer wells, adding uncertainty to the analysis. For the industrial sites, groundwater concentrations remain high in the release areas, even though releases likely began many decades ago. These conditions suggest a continual source contribution from NDMA held in site soils or in the vadose zone or demonstrate that continuing activities are still releasing NDMA. Sites for recycled water are also viewed as continuous releases from the time that the first release began until NDMA was removed from the source water. Table 2.2 summarizes the estimated time of the first NDMA release at each of the six sites. The diamonds correspond to the sites listed in the order depicted in Table 2.1 (e.g., the first releases of NDMA at the San Gabriel Valley Baldwin Park OU are believed to have occurred in 1943, while releases at the Rancho Cordova Aerospace Facility began in the early 1950s).

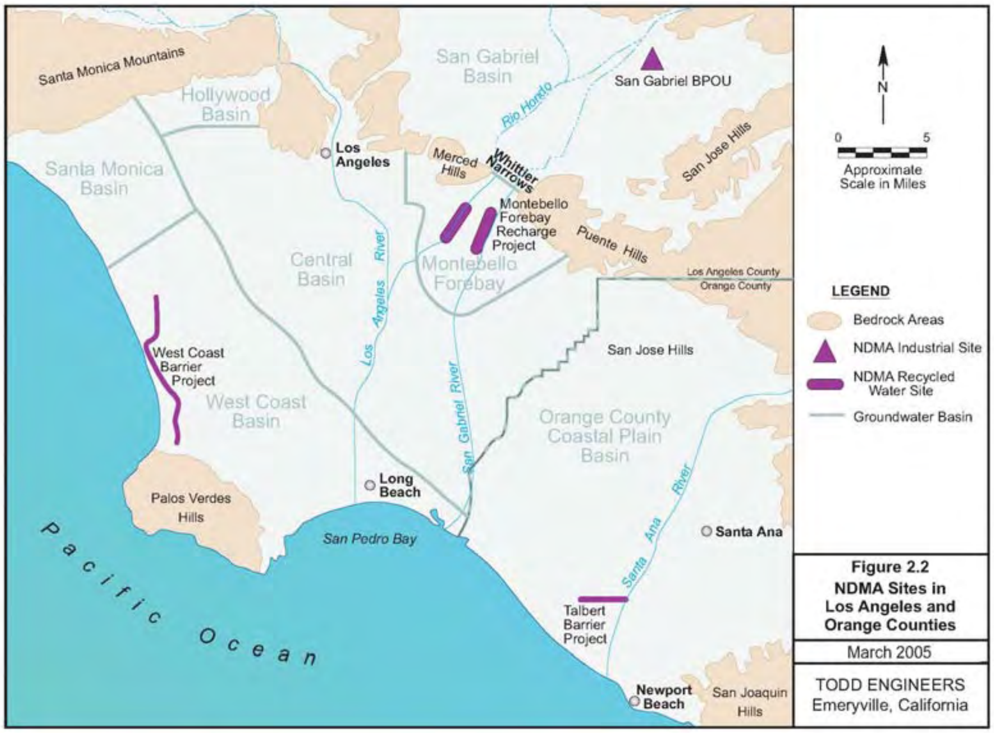
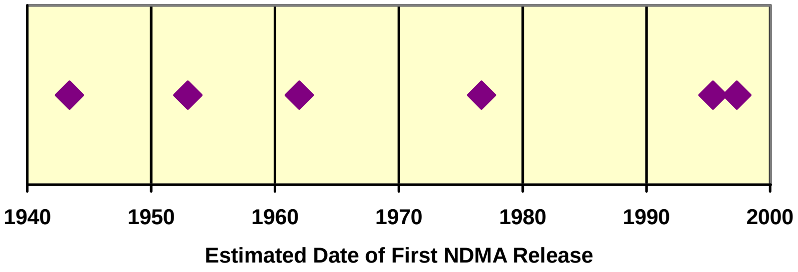


**Figure 2.2. NDMA Sites in Los Angeles and Orange Counties.**

## Table 2.2. Timing of NDMA Release at Selected Sites



## 2.3 FATE AND TRANSPORT PROCESSES IN THE SATURATED ZONE

When a dissolved constituent (such as NDMA in wastewater) is introduced into the saturated zone, the mass of that constituent begins to spread throughout the aquifer. This spreading occurs in three dimensions and results in decreasing concentrations in groundwater with distance from the release. The amount of spreading is influenced by a variety of factors relating to the aquifer (geologic heterogeneity), groundwater flow regime (e.g., hydraulic gradients and geometry of the basin), and properties of the constituent (e.g., reactivity). The distribution of mass in the groundwater system at any given time is often represented by contour lines of equal concentrations, known as plume maps.

In general, mass is spread by the existing groundwater flow patterns that transport mass in a downgradient direction. This process, referred to as advection, is the dominant transport process of mass in the groundwater system. Advection will transport NDMA source water at different rates in different strata because of heterogeneity inherent in most aquifers. As a result, the concentration measured in a downgradient well will not likely contain the same concentration as originally measured in the source water, even if other transport mechanisms that spread the constituent are ignored.

Mass can also be spread across advective flowlines through the process of dispersion. Dispersion is the physical spreading of mass throughout the groundwater system, lowering concentrations but causing a larger area of impact. The process occurs as two fluids (e.g., source water and native groundwater) flow past one another and replace each other. Dispersion controls solute transport at many scales, from pore size distribution to geologic layering. Heterogeneities in the aquifer cause this physical spreading to occur in three dimensions: longitudinal (parallel to groundwater flow), transverse (normal to groundwater flow), and vertical. Dispersion is expected to be a factor in controlling concentrations of NDMA in the aquifer. For purposes of this report, dispersion is viewed as a natural process controlled by aquifer heterogeneity and groundwater flow patterns. Spreading of mass through induced lateral or vertical gradients by nearby pumping wells is not considered to be dispersion. However, the mixing or diluting of mass by pumping is expected to be an important process in spreading NDMA mass and decreasing concentrations in groundwater wells.

Mass is also spread by diffusion, a chemical process by which mass moves on a molecular scale from areas of high concentration to areas of lower concentration. This movement is controlled by the concentration gradient and will occur even if the water is not moving. The rate of diffusion is slowed by the aquifer materials in the saturated zone as mass moves through the pore spaces and around the sand particles. Because of the movement of mass, the solute will spread out away from the source, decreasing concentrations in the water where it is introduced. However, this process of mass transport occurs very slowly and is more important in low-permeability aquifers (Todd and Mays, 2005). As such, diffusion is not expected to be a controlling process for mass redistribution in the aquifer at the scale of this study.

In addition to spreading in the aquifer, mass can be temporarily or permanently removed from the flow system. Reactions between the constituent and aquifer materials can cause mass to be sorbed onto aquifer particles, attenuating or retarding mass movement in the groundwater system. A chemical's mobility in soil and groundwater is, in part, dependent on whether it will likely partition out of the aqueous phase or be sorbed onto particles in soil or sediments.

The capacity for sorption is expressed as two coefficients, $K_{OW}$ and $K_{OC}$, which reflect properties of the chemical.

The octanol water partition coefficient, $K_{OW}$, is defined as the ratio of an organic chemical's concentration in octanol (a solvent) to its concentration in water. It is used to relate a chemical's ability to partition (separate) itself between an organic phase (e.g., sorption in sediment) and an aqueous phase. Chemicals with very low $K_{OW}$ values (e.g., <10) are considered hydrophilic (does not partition out of water); those with $K_{OW}$ values greater than 104 are considered very hydrophobic (partitions out of water) (International Water-Guard 2002; Lenntech, 2004). An additional measure of a chemical's mobility in organic soils is the organic carbon to water partition coefficient ($K_{OC}$). The $K_{OC}$ measures a chemical's ability to partition between solid and solution phases in saturated soils. It is an experimental measurement of a chemical's sorption to soil organic carbon and therefore measures mobility in soil (Lyman et al., 1990).

The range of $K_{OC}$ reported for NDMA is approximately 12, and the reported $K_{OW}$ is 0.269. The value of $K_{OC}$ measured in landscape soils (see section 3.2) ranges from 68 to 118. All of these values are relatively low for these coefficients. Given NDMA's relatively low $K_{OW}$ and $K_{OC}$, sorption is not expected to be a controlling factor for NDMA fate and transport in the saturated zone.

Mass can be removed permanently from the groundwater system through chemical reactions or bacteria (chemical or biotransformation). Very little is known about the chemical and biological transformation of NDMA in the saturated zone. Experimental studies associated with this research project are some of the first studies focused on this issue. Preliminary data indicate that aerobic conditions (presence of oxygen) are more likely to result in biodegradation (Howard et al., 1991; Liteplo et al., 2002). The transfer of oxygen in the groundwater system is conducted by oxidation–reduction reactions (redox). Redox levels in the groundwater system are a balance between the introduction of oxygen into the system (typically through surface recharge) and the consumption of oxygen (typically by bacteria) (Drever, 1988). Variables that control this balance in groundwater are the following:

- Oxygen content of recharge water
- Distribution and reactivity of organic matter
- Distribution of potential redox buffers in the aquifer
- Circulation rate of groundwater (Drever, 1988)

These conditions are expected to be highly variable, both with depth and distance in the natural groundwater system. The injection of surface water and/or recycled water could change the redox of the natural system by adding various amounts of oxygen and/or carbon to the groundwater. Redox conditions were found to be more oxidizing in aquifers along a bank of injection wells in Southern California than in native groundwater (CH2M Hill, 2003). These variables indicate that both favorable and unfavorable conditions for NDMA biodegradation can coexist in the same aquifer.

## 2.4 SAN GABRIEL VALLEY BALDWIN PARK OPERABLE UNIT

### 2.4.1 Introduction

Groundwater contamination in the San Gabriel Valley has been investigated since 1979, when contaminants were detected in a water supply well. The investigation identified large areas where groundwater had been impacted with chlorinated solvents and led to the placement of the entire valley on the National Priorities List (NPL) in 1984. The NPL site was the nation's largest Superfund site and was divided into Operable Units based on source areas, groundwater flow, and the mapping of basin-wide plumes of contamination. The Baldwin Park Operable Unit (BPOU) was delineated in the northeastern portion of the San Gabriel Valley Groundwater Basin (Figure 2.2).

In 1999 and 2000, additional contaminants including NDMA were identified in the BPOU. NDMA was detected in a shallow monitoring well at an aerospace facility that had conducted rocket testing and other operations that involved NDMA. This facility is considered the NDMA source area and is identified by the triangle in Figure 2.2. Additional sampling indicated that NDMA had migrated downgradient and impacted groundwater throughout the BPOU. Publicly available data were compiled and analyzed to document the NDMA impact and examine the fate and transport of NDMA in groundwater.

### 2.4.2 Available Data

USEPA maintains a basin-wide database of NDMA and other contaminants detected in groundwater. The database can be downloaded and queried by using database software. The database contains more than 1 million chemical records for 1820 wells in the basin. NDMA data have been compiled for more than 700 wells in the basin, 168 of which were in the BPOU (wells with dual completions were counted as two wells).

NDMA data were from production wells, industrial facility monitoring wells, and USEPA-installed monitoring wells. Twelve of the wells in the BPOU are multiport monitoring wells that are constructed with 3 to 13 separate sampling ports. These ports sample groundwater at discrete vertical intervals throughout the water column.

The database was downloaded from USEPA and used to define the areal and vertical distribution of NDMA concentrations in groundwater. In addition, key documents were reviewed from files of the USEPA and the Regional Water Quality Control Board, Los Angeles Region (LARWQCB), regarding contaminant use and site investigations at the NDMA site. A list of references is provided at the end of this report.

### 2.4.3 Hydrogeologic Setting

The BPOU site is located in the western portion of the San Gabriel Valley Groundwater Basin along the San Gabriel River (Figures 2.2 and 2.3). The basin is surrounded by bedrock highs and geologic faults. Basin sediments have not been differentiated into separate aquifer units, given the lack of continuous aquitards in the BPOU subsurface. Basin sediments extend to depths of more than 1500 ft in the central portion of the BPOU.

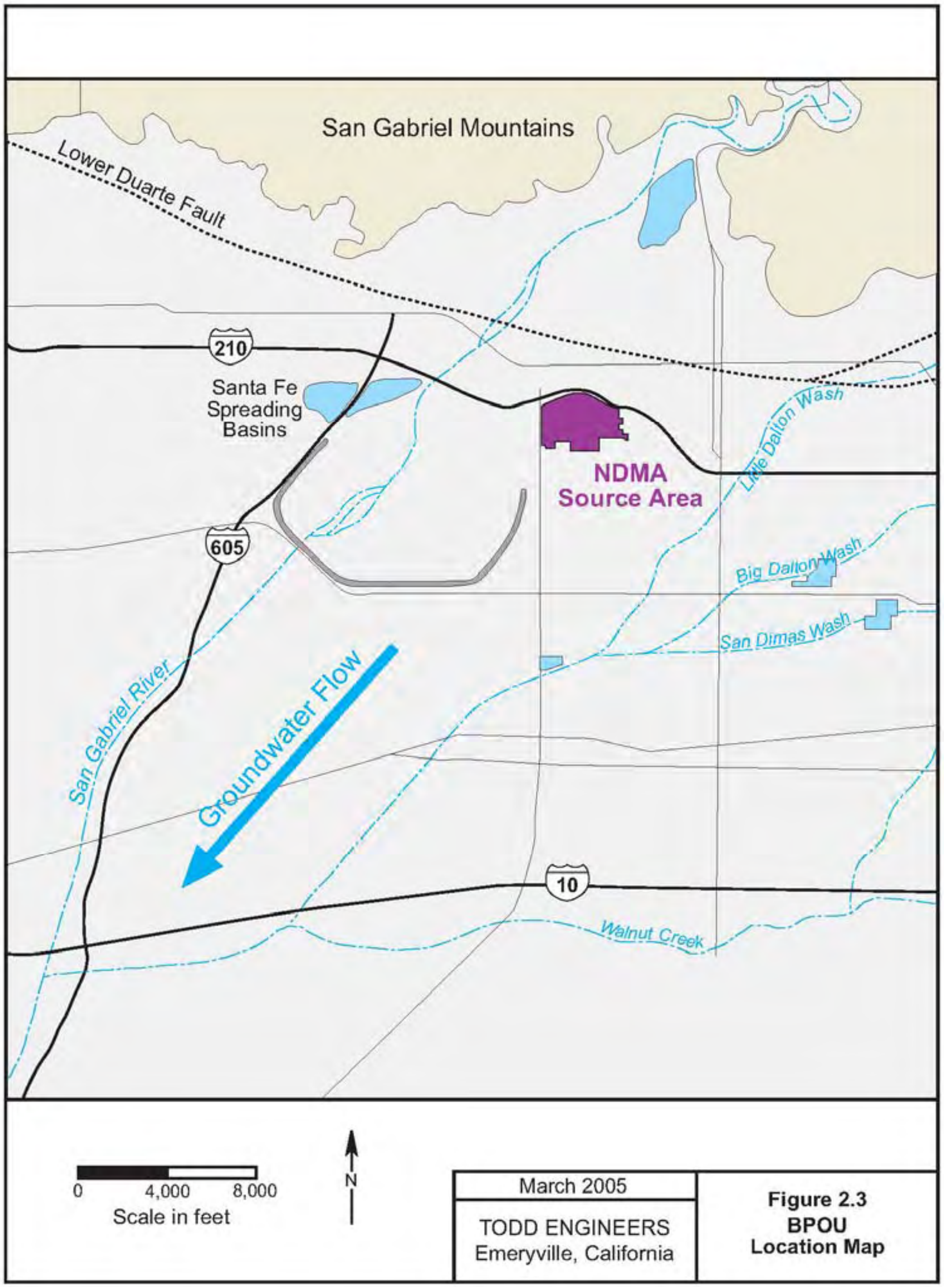


**Figure 2.3. BPOU Location Map.**

The basin receives natural recharge from precipitation and streamflow originating in the San Gabriel Mountains to the north. Imported surface water from the State Water Project and the Colorado River is also used to recharge groundwater through permeable river channels and a series of recharge basins located mainly along the San Gabriel River. Groundwater discharge occurs by pumping of water supply wells and the natural subsurface outflow at Whittier Narrows (WN). At WN, groundwater flows into the Montebello Forebay (Figure 2.2).

Groundwater occurs under unconfined and semiconfined conditions. Beneath the source area, the water table is relatively deep. Water levels occur at an average elevation of about 250 ft above mean sea level (msl) beneath the site but have been as high as about 330 ft msl in the past. If one uses an average ground surface elevation of 550 ft msl, the water table is about 200 to 300 ft beneath the NDMA source area.

Groundwater generally flows from the surrounding uplands toward the basin center and then southwesterly toward the basin outflow. In the BPOU, the average groundwater flow direction is to the southwest as shown by the arrow in Figure 2.3, but groundwater flow is more complex in the vicinity of the NDMA source area. Artificial recharge operations at nearby spreading basins create groundwater mounding and fluctuations in groundwater flow directions. These fluctuations occur on a seasonal and drought-cycle scale and result in groundwater flowing to the west, southwest, south, and southeast at various times. This dynamic condition results in widely variable contaminant concentrations in wells, depending on whether the plumes are flowing toward or away from a well at any given time. Groundwater pumping in the BPOU also contributes to the dynamic nature of the groundwater basin and creates strong vertical gradients in some areas. These vertical gradients have resulted in the spreading of NDMA mass and other contaminants to significant depths in the BPOU.

Locally, the aerospace facility rests on the very permeable alluvial fan deposits of Recent age. These deposits are locally mined for sand and gravel and contain boulders, cobbles, gravel, and sand with only minor percentages of silt and clay. Very little organic matter has been detected in site soils. Sediments are older and slightly finer-grained in the groundwater system but are also highly permeable. Nearby water supply wells sustain production rates of 2000 to 3000 gal per min (gpm), demonstrating the permeable nature of the deposits. Hydraulic conductivity values are estimated to be between 200 and 300 ft per day in the upper basin alluvium (CH2M Hill, 1993).

### 2.4.4 NDMA Site Use

The aerospace facility associated with NDMA consists of a 125-acre site located within the BPOU, about 1.5 mi east of the San Gabriel River (Figure 2.3). Rocket fuel and rocket motor operations began at the site around 1943 and continued to about 1968 (CH2M Hill, 1990). Industrial operations have continued at the site but have focused more on research, development, and production of electronics than on aerospace-related activities (Harding Lawson, 2001).

USEPA has documented use and past disposal practices of hazardous waste at the site (CH2M Hill, 1990). Liquid fuel composed of aniline, furfuryl alcohol, gasoline, xylidene, jet fuel, hydrazine, and nitromethane was used in site operations. Liquid wastes were discharged through drainage channels into unlined leach beds, leach pits, and septic tanks (prior to sewer hook-up in the 1950s). Propellants were spilled on the ground during rocket tests due to leakage from corroded containers, discharge of unburned propellant from rockets, rinsing of propellant systems, and flushing of test bay areas (CH2M Hill, 1990).

NDMA is associated with the rocket fuel mixture unsymmetrical dinethyhydrazine (UDMH) either as an impurity or a combustion byproduct. Potential NDMA source areas on the site included various drainage courses, leach beds, former drum storage areas, former ponded liquid areas, waste treatment facilities, and the pilot plant and distillation unit for UDMH.

Spills and disposal of NDMA-impacted liquid on the land surface would have infiltrated permeable site soils and percolated through the vadose zone to underlying groundwater.

Groundwater is relatively deep at the site, and NDMA source water would have to migrate vertically 200 to 300 ft to reach groundwater. Transport times through the vadose zone would be highly variable, depending on then-current site conditions, but could be on the order of days. A substantial amount of NDMA source water apparently reached groundwater and continues to be released from the vadose zone to groundwater, as evidenced by the widespread detections and continuing detections near the source. The continued release could be attributable to the relatively large amount of NDMA released at the site or to some aspect of the local geology that favors NDMA retention in the vadose zone.

### 2.4.5 NDMA in Source Water

There are no data available to estimate NDMA concentrations in source water. In addition, the volumes of water or timing of releases is unknown. Releases at the surface likely began more than 60 years ago and continued for an unknown length of time, possibly up to 25 years.

A shallow monitoring well located in the UDMH distillation source area has detected NDMA at the highest concentrations seen in BPOU wells. The well continues to detect NDMA at very high concentrations, even though NDMA releases at the surface have ceased. Although it is acknowledged that these detections are likely lower than levels in the source water, perhaps orders of magnitude lower, they provide a minimum NDMA concentration for source water at the site. NDMA has been detected consistently in this well at concentrations up to 14,000 ng/L with an average concentration of 3670 ng/L. These data are provided in Figure 2.4.

### 2.4.6 NDMA in Groundwater

USEPA compiled NDMA data for 168 wells in the BPOU. NDMA was detected in at least one groundwater sample from 47 of these wells. Laboratory detection limits varied from about 30 ng/L to 2 ng/L. As previously discussed, the highest NDMA concentrations have been consistently detected in a shallow monitoring well at the source area at a maximum concentration of 14,000 ng/L and an average concentration of 3670 ng/L. NDMA concentrations are consistently detected above 1000 ng/L (same order of magnitude as the average NDMA concentration in the source area) up to several miles downgradient.

Given the dynamic groundwater system and the variable detection levels, NDMA detections appear to be sporadic in many wells. Even wells with typical concentrations above 100 ng/L will often have a few samples where NDMA was not detected. In order to evaluate these variable concentrations, the spatial distribution of NDMA was mapped. Figure 2.5 shows the NDMA plume map. Plume mapping used the average values from more than 100 wells sampled from 1998 through 2003. For multiport wells, average values from the port with the highest concentration were used. If a well had detected NDMA in one or more sampling events, detections were averaged and nondetects were not used. This methodology likely results in a map that represents the maximum area of NDMA impacts.

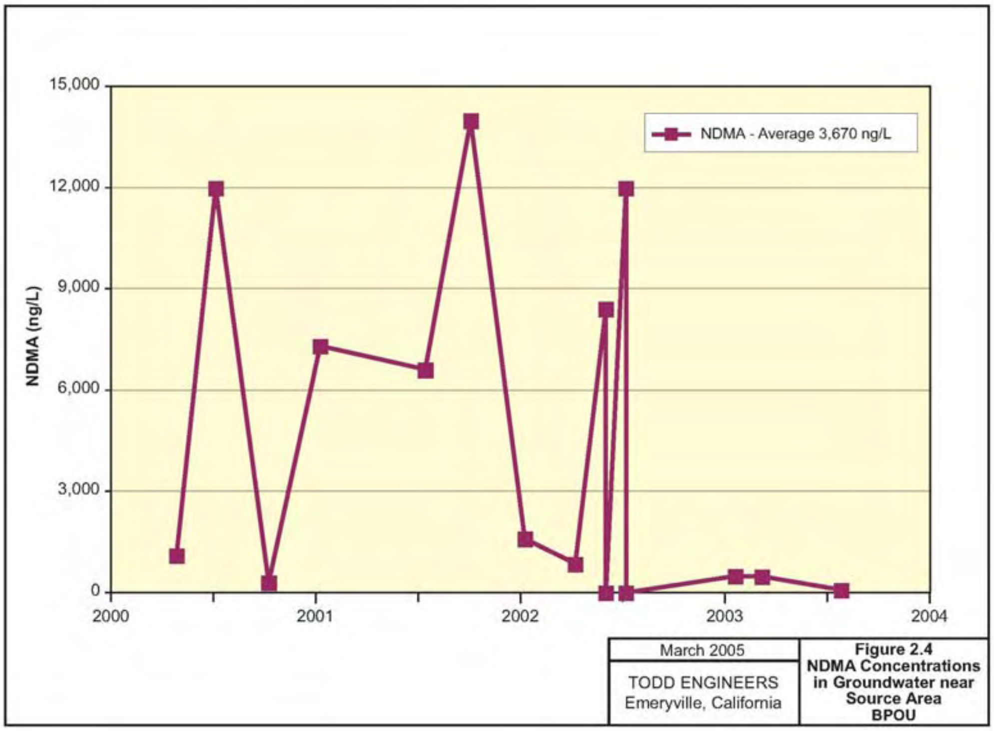


**Figure 2.4. NDMA Concentrations in Groundwater near Source Area, BPOU.**

Plume concentrations are highest at the source area and decrease downgradient. As shown in Figure 2.5, NDMA concentrations above 1000 ng/L extend more than 2 mi downgradient. Concentrations above 50 ng/L extend a distance of 7.2 mi downgradient from the source area. Concentrations between 2 and 50 ng/L were considered less certain and not mapped past the BPOU map area. However, as indicated in Figure 2.5, NDMA detections extend further downgradient and likely create a total plume length of more than 8 mi. These distances are consistent with a release in the mid-1940s and an average groundwater velocity of about 2 ft per day, a rate consistent with other groundwater velocity calculations in the BPOU (GeoSyntec Consultants and Todd Engineers, 1995).

The narrowness of the plume near the source area indicates that transverse dispersion is not an important factor in spreading NDMA in that area. However, concentrations are spread laterally in the southern portion of the plume as a result of production wells that pump groundwater close to the plume edge.

The vertical distribution of NDMA is illustrated by the cross section in Figure 2.6. This cross section extends from the source area to the southwestern edge of the map along the centerline of the plume. Average values are posted beside the well screens. If a well detected NDMA in some samples but not others, both results are posted and the detection is usually used in contouring. One exception is the deep detections in Well EPA 5-1. Data for other constituents indicated that detections in these ports might be artifacts of the well installation at this location.

As indicated in the cross section, NDMA has been spread vertically throughout the aquifer. Data indicate that NDMA has been detected more than 700 ft below the water table.

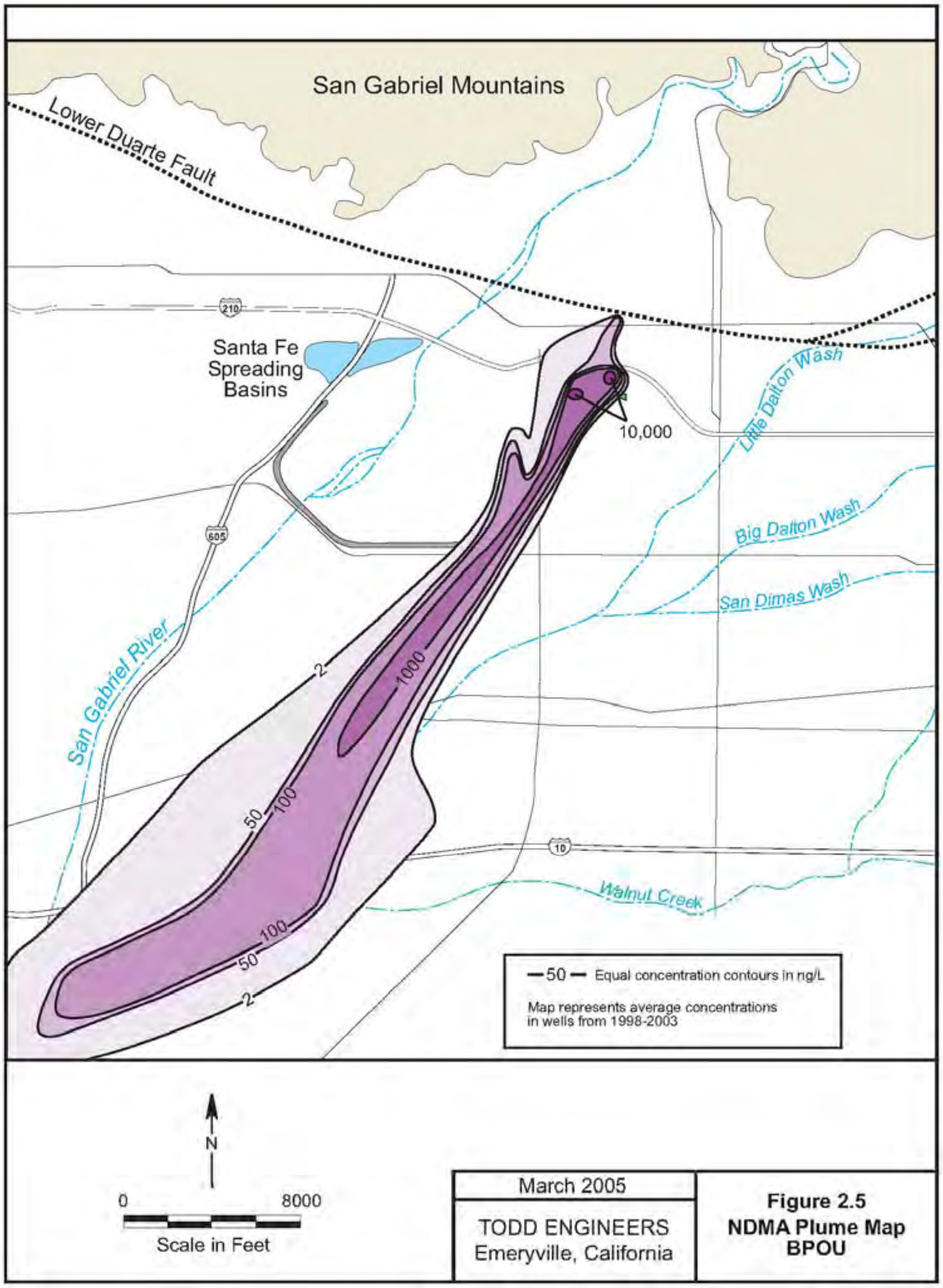


Figure 2.5. NDMA Plume Map, BPOU.

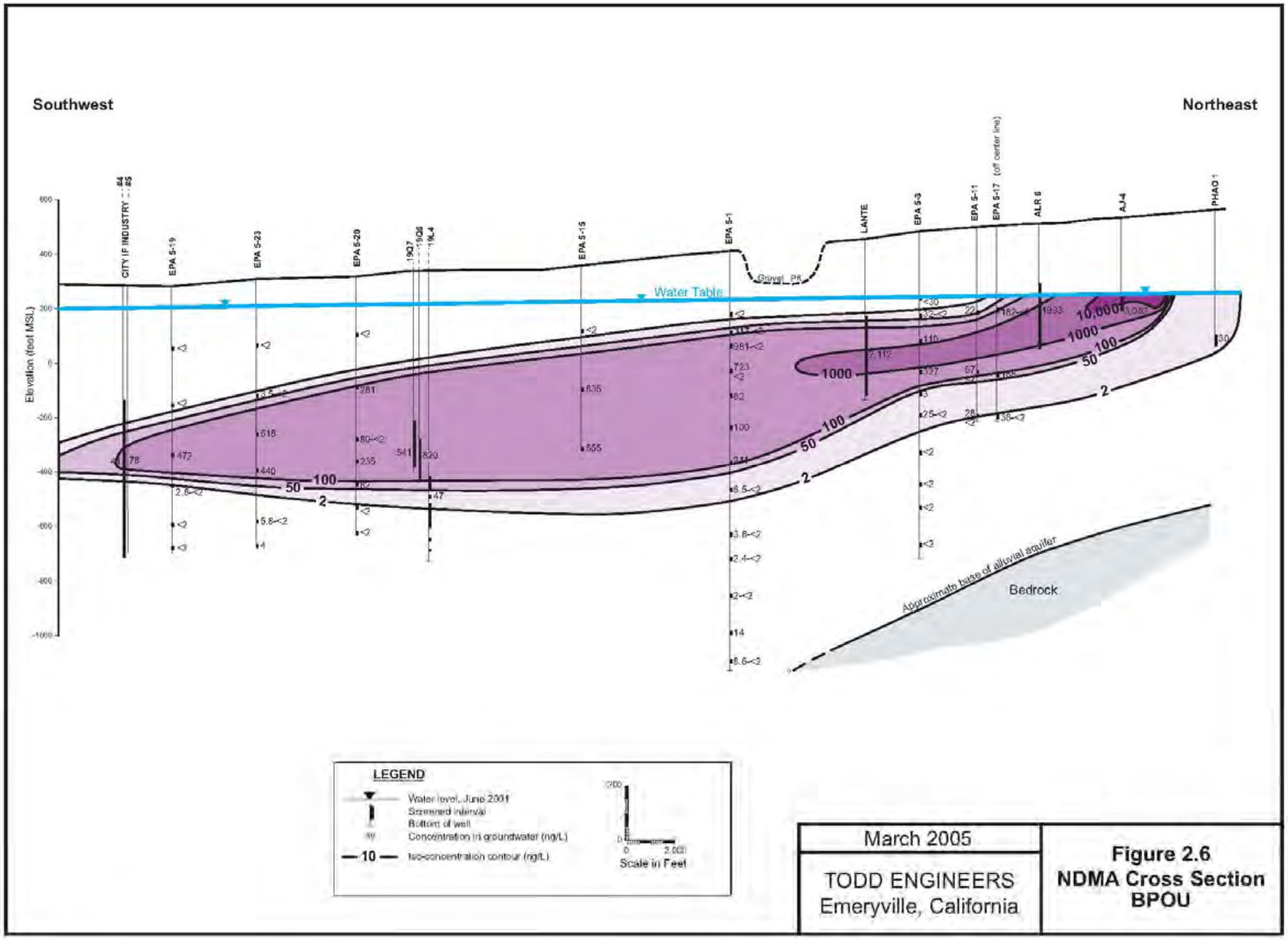


Figure 2.6. NDMA Cross Section, BPOU.

### 2.4.7 NDMA Fate and Transport

Since so little is known about the original NDMA releases, it is not possible to determine if significant mass has been removed from the system based on plume maps alone. In order to further evaluate NDMA in the BPOU, the occurrence in groundwater has been compared to the occurrence of perchlorate, another groundwater contaminant in the BPOU.

Perchlorate ($ClO_4^-$) is also a component of some rocket fuels and is associated with rocket-testing activities. Perchlorate has been detected in site soils near the UDMH distillation unit. The highest concentrations of perchlorate in groundwater are detected in the same well that also detected the highest concentrations of NDMA. Perchlorate is miscible in groundwater and considered to be a relatively conservative tracer of groundwater flow. Data regarding the possible degradation of perchlorate indicate either no significant degradation in groundwater or degradation under conditions significantly different from those conducive to NDMA degradation.

Figure 2.7 shows a map of perchlorate concentrations in groundwater. The perchlorate plume is generally coincident with the NDMA plume (Figure 2.5), although concentrations are different by about 1 order of magnitude (note the different units). In a comparison of the two plumes, both are relatively narrow in the source area and spread laterally in the southern portion of the maps. The perchlorate plume does not appear to extend as far downgradient as NDMA, but that trait is likely a function of the different contour intervals used for the two maps. Also, because NDMA is being analyzed at much lower detection levels, weaker concentrations can be detected.

Figure 2.8 is a graph of perchlorate and NDMA concentrations in groundwater for time periods when both chemicals were sampled. Data are from the source area monitoring well. When perchlorate and NDMA data are plotted together, concentrations appear to covary over time. This indicates that changes in concentration are controlled by changes in the groundwater system and not changes in source concentrations of the chemicals (which would not be expected to covary).

Since plumes are coincident and concentrations in the source area appear to covary, downgradient decreases in NDMA and perchlorate should be similar on a percentage basis if they are both being controlled by the same fate and transport properties. To test this hypothesis, five wells were selected along the centerlines of the two plumes to compare downgradient concentrations. Concentrations (in micrograms per liter) for NDMA and perchlorate for these wells are plotted with distance from the source area in Figure 2.9 on a semi-log scale.

As shown on the graph, the slopes of the two lines are similar to distance downgradient from the source. This indicates that the two chemicals are decreasing in concentration at approximately the same rate. Since perchlorate is not expected to degrade under the same conditions as NDMA, it can be inferred that decreases are controlled by advection, dispersion, and spreading by pumping wells rather than by degradation.

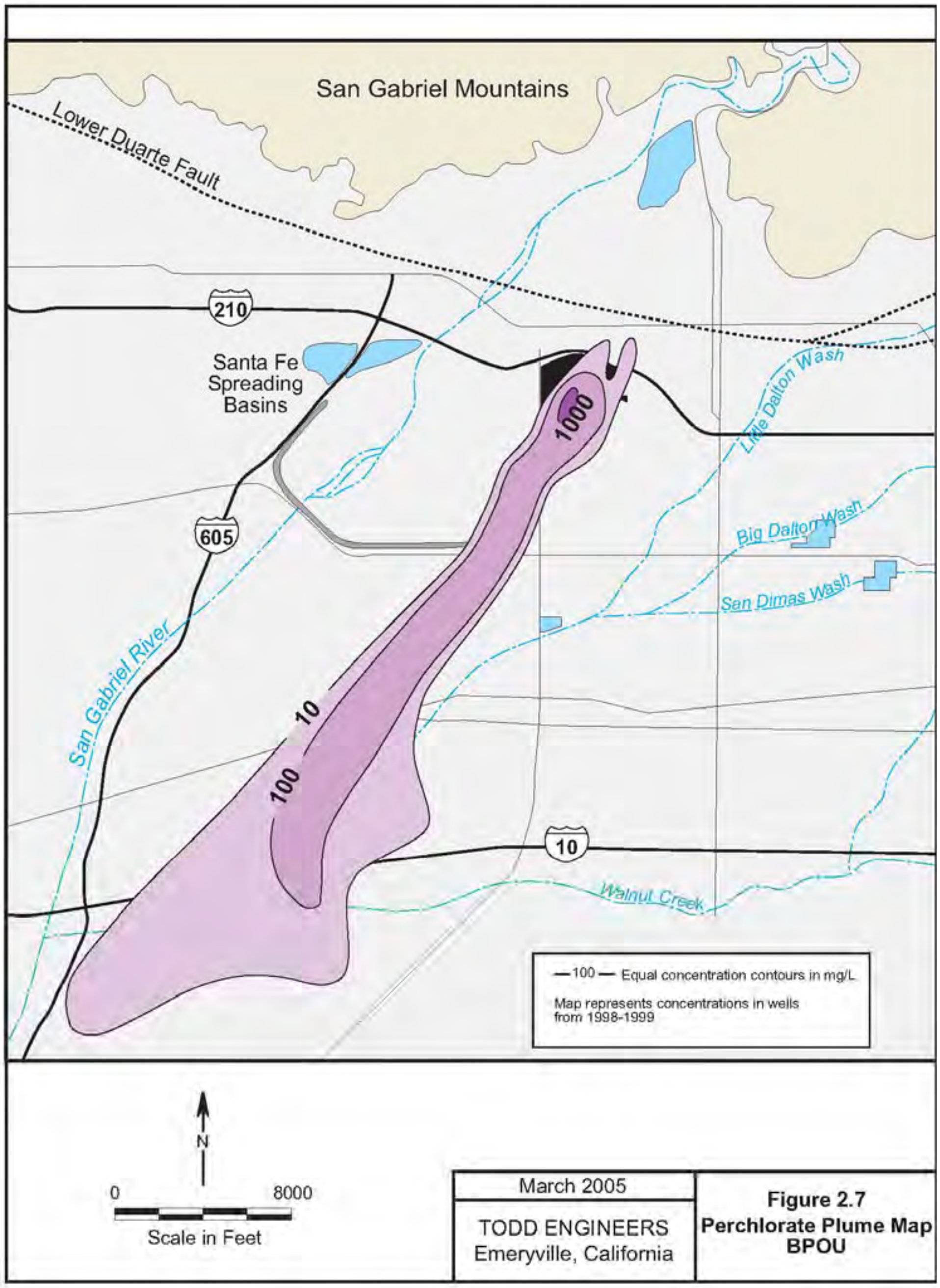


**Figure 2.7. Perchlorate Plume Map, BPOU.**

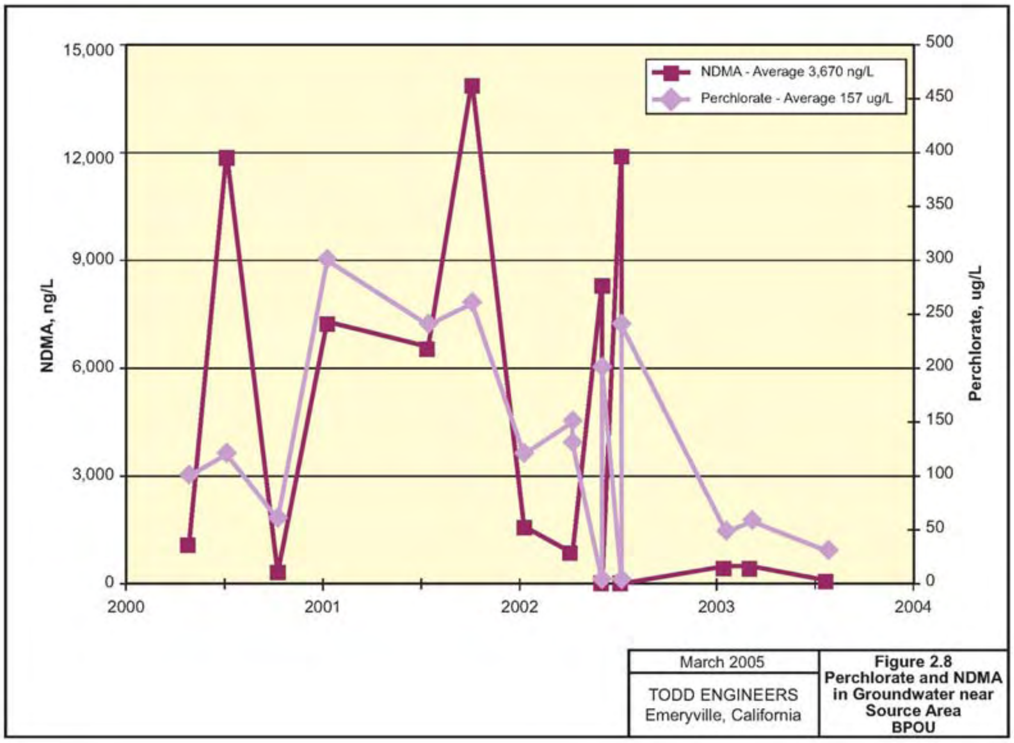


**Figure 2.8. Perchlorate and NDMA in Groundwater near Source Area, BPOU.**

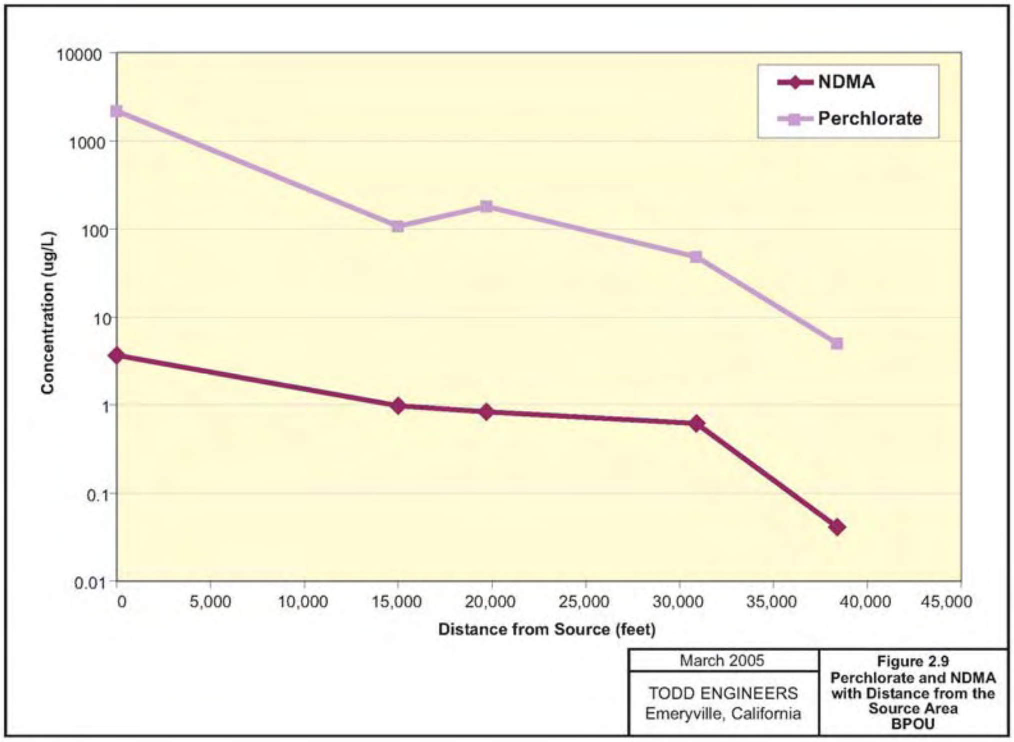


**Figure 2.9. Perchlorate and NDMA with Distance from the Source Area, BPOU.**

### 2.4.8 NDMA Fate and Transport Summary

*NDMA Detections*

- NDMA concentrations in source water released in the BPOU are not known. Data from a shallow monitoring well near the source area indicate NDMA concentrations up to 14,000 ng/L, with an average concentration of 3670 ng/L.
- NDMA was detected in at least one groundwater sample in 47 wells in the BPOU.
- NDMA concentrations are consistently detected above 1000 ng/L up to several miles downgradient. NDMA concentrations above 50 ng/L persist 7.2 mi downgradient. NDMA concentrations below 50 ng/L extend further downgradient and may indicate a total plume length of more than 8 mi.
- NDMA concentrations plotted on a cross section indicate that NDMA mass has spread significantly in the vertical direction and is detected at depths greater than 700 ft below the water table.

*NDMA Fate and Transport in BPOU Groundwater*

- Since NDMA concentrations in source water released in the BPOU are not known, NDMA degradation that occurred in the vadose zone cannot be documented.
- NDMA persists more than 8 mi downgradient of the source area. The plume length is consistent with reasonable release times and groundwater velocities.
- The persistence of concentrations within the same order of magnitude for miles downgradient indicates that NDMA is not being significantly degraded.
- NDMA mass has been spread vertically to depths of more than 700 ft below the water table due to pumping of deep production wells.
- A comparison of concentrations for NDMA and perchlorate in various distances from the source indicates that concentrations are decreasing at the same rate. This observation indicates that NDMA is not being degraded significantly, since perchlorate is not expected to be significantly degraded or is degraded under conditions different from those for NDMA.

## 2.5 RANCHO CORDOVA AEROSPACE FACILITY

### 2.5.1 Introduction

NDMA use and disposal have been documented at an industrial site on the east side of the Sacramento Valley of Northern California (Figure 2.1). Operations on the site have included the production and testing of liquid rocket fuel engine systems, a process associated with NDMA. NDMA impacts to groundwater beneath the site are documented in publicly available reports and data.

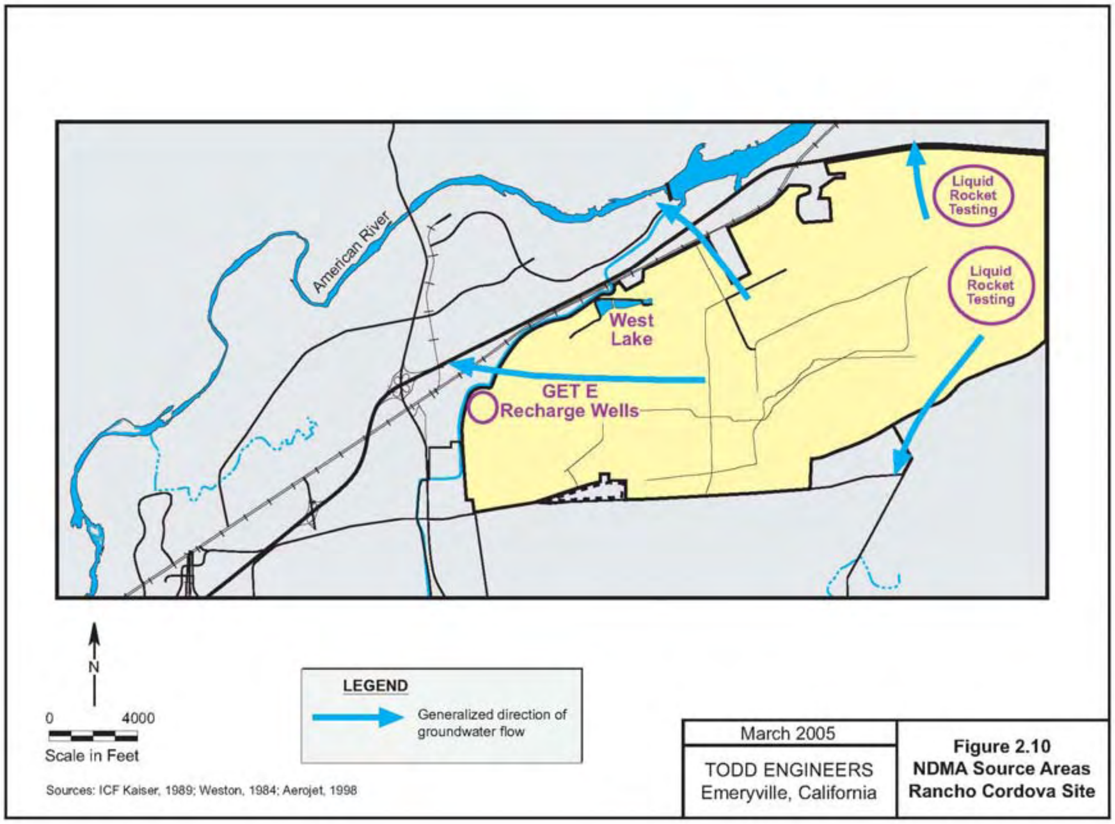
Groundwater contamination has been investigated at the site since the early 1980s, when chlorinated solvents were detected in site monitoring wells. Since that time, groundwater contamination has been more fully characterized, and remedial actions have been implemented. In 1998, additional investigations of NDMA were conducted. New areas of NDMA impacts were identified based on laboratory methods with lower detection levels than had previously been available. Data and reports on these impacts were reviewed for this report. NDMA releases and impacts to groundwater are described with respect to the fate and transport of NDMA in groundwater.

### 2.5.2 Available Data

More than 3000 monitoring wells have been installed both on and off the Rancho Cordova site. Sampling results from these wells are compiled into an electronic database by the site owner and submitted to regulatory agencies, including the Regional Water Quality Control Board, Central Valley Region (CVRWQCB). This database contains more than 1 million records and includes sampling results for NDMA. Site investigation reports that document NDMA impacts to groundwater are also submitted to the CVRWQCB and are available for public review. The electronic database and key documents were reviewed for this report. These data were supplemented by regional investigations on the groundwater hydrology conducted by the California Department of Water Resources (DWR) and the U.S. Geological Survey (USGS). A list of references is provided at the end of this report.

### 2.5.3 Hydrogeologic Setting

The Rancho Cordova facility is located on an 8000-acre site south of the American River and 15 mi east of Sacramento (Figure 2.10). The site is on the eastern edge of the Sacramento Valley near the transition zone between bedrock of the Sierra Nevada and the valley-fill sediments to the west.



Sources: ICF Kaiser, 1989; Weston, 1984; Aerojet, 1998

**Figure 2.10. NDMA Source Areas, Rancho Cordova Site.**

Subsurface geology consists of unconsolidated to consolidated sedimentary units of Miocene to Recent age. More permeable layers in these units are the aquifers tapped by local water supply wells. Aquifers have been identified in the following geologic units, listed in order of increasing depth: Riverbank Deposits, Laguna Formation, Mehrten Formation, and Valley Springs Formation. Groundwater contamination is found mainly in the Laguna and Mehrten formations. Investigators have delineated aquifers as A, B, C, D, E, and F. The main aquifers extend to about 400 ft below the central portion of the site (about 200 ft below msl) and deepen to the west.

Groundwater occurs under unconfined and semiconfined conditions in the area. Groundwater flow is regionally to the southwest, generally paralleling the American River channel. However, groundwater flow directions are controlled locally by production wells and other factors. Shallow bedrock beneath the eastern portion of the site results in a semiradial groundwater flow pattern beneath the site. At various portions on the site, groundwater can flow north, northwest, west, or southwest (see generalized flow direction indicated by the arrows in Figure 2.10). Hydraulic conductivity ($K$) varies over the site and in aquifer layers; estimates in the central and western portions of the site indicate $K$ values of about 40 ft/day. Estimates of groundwater flow velocity in that area range from about 1 to 2.3 ft/day.

### 2.5.4 NDMA Site Use

Although numerous activities have been conducted at the Rancho Cordova site over the years, primary operations involved the manufacturing and testing of liquid and solid rocket engines. NDMA is associated with the rocket fuel mixture UDMH and occurs both as a component in liquid rocket fuel and a combustion byproduct of the firing of liquid-fueled rocket engine systems (Aerojet, 1998).

Four major source areas (Figure 2.10) have been associated with NDMA impacts to groundwater including the following:

- Liquid rocket testing on the southeastern portion of the site
- Liquid rocket testing on the northeastern portion of the site
- Disposal of liquid wastes into surface water ponds, referred to as West Lake, on the northwestern portion of the site
- Injection of effluent from a groundwater extraction and treatment (GET) facility, referred to as GET E, on the western portion of the site

NDMA impacts to groundwater have been documented in each of these areas. NDMA has also been detected at other source areas around the site, but groundwater impacts appear to be more limited than those associated with the four main areas listed above (Aerojet, 1998; Roy F. Weston, Inc., 1984; ICF Kaiser, 1989).

When groundwater contamination was detected in the late 1970s and early 1980s, site owners took steps to remediate the problem. GET facilities were installed around the perimeter of the site beginning in about 1983. These GET facilities were originally designed to treat contaminants other than NDMA, and as a result, NDMA remained in the effluent in areas where groundwater had already been impacted. At the GET E facility on the western boundary of the site, treated groundwater that contained NDMA was inadvertently reinjected into the aquifers via injection wells. This reinjection created an additional NDMA plume in groundwater beginning with the completion of injection wells in 1983.

### 2.5.5 NDMA in Source Water

NDMA concentrations in source water (i.e., spills or disposal) were not researched specifically for this study but are not likely to be sufficiently characterized. Chemical data are generally unavailable for site wastewater. Releases in the source areas likely occurred at the surface more than 45 years ago and continued for an unknown length of time.

The highest NDMA concentrations in known source areas are detected in the eastern portion of the site, where liquid rocket testing was conducted (Figure 2.10). Many wells in this area have detected NDMA concentrations that exceed 10,000 ng/L in groundwater. Even though NDMA concentrations in the source water (or waste rocket fuel) were obviously very high, source water concentrations cannot be estimated from available data. Without some information on the source water, few inferences can be made about the fate and transport of the NDMA-impacted source water in groundwater.

However, NDMA concentrations in source water are quantifiable for at least one of the areas impacted. NDMA has been detected in the treatment plant effluent of GET E at 250 ng/L (Aerojet, 1998) (Figure 2.10). This effluent has been reinjected into the groundwater system since the mid-1980s and forms a groundwater plume in that area.

Data dating back to 1983 indicate an average NDMA concentration of 171 ng/L from GET E extraction wells (CVRWQCB, 2004). These data provide a reasonable source term for the NDMA plume on the western portion of the site. Since these data represent the best estimate of source concentrations for any of the impacted areas, the analysis of fate and transport focused on this plume.

### 2.5.6 NDMA in Groundwater

Figure 2.11 shows the general areas of groundwater that have been impacted by NDMA at the site. Plume maps consider concentrations from all aquifers and represent a composite area of impact. Not all aquifers are similarly impacted beneath the plume areas. Three main plumes of NDMA in groundwater are delineated, two on the east and one on the west (Figure 2.11). All plumes are consistent with groundwater flow directions in the respective areas. The two plumes on the east are presented schematically and represent only the main area of impact. The western plume is taken from plume maps prepared by the site owner (Aerojet, 2000). Smaller plumes in the west are also taken from site owner maps.

The plume on the northeastern portion of the site contains concentrations in groundwater above 10,000 ng/L but appears to be contained on the site property by extraction wells (Figure 2.11). A second plume of groundwater contamination on the southeastern portion of the property also contains wells with NDMA concentrations exceeding 10,000 ng/L. NDMA in this area appears to have migrated more than 1 mi offsite to the south (Figure 2.11). NDMA concentrations above 1000 ng/L persist along most of the length of the plume and suggest that NDMA is not being significantly degraded.

The western NDMA plume has also migrated offsite (Figure 2.11) and has been detected in two offsite water supply wells at concentrations of 150 ng/L and 78 ng/L. NDMA in this plume may have originated as wastewater disposed in the ponds of West Lake; a groundwater monitoring well at the ponds has detected NDMA at a concentration of 1300 ng/L (Aerojet, 1998).

Groundwater extraction wells associated with the GET E facility have intercepted some of this water and reinjected it into the groundwater system along the western property boundary (Figures 2.10 and 2.11). As previously discussed, NDMA concentrations have been detected in this water at 250 ng/L and have averaged about 171 ng/L in nearby wells since the early 1980s. The western plume of Figure 2.11 is likely a composite of groundwater impacts from West Lake and injection wells. Water was injected into wells in the GET E area beginning in 1983.

## 2.5.7 NDMA Fate and Transport

The western NDMA plume appears to have migrated a distance of 8000 to 10,000 ft from the source area in approximately 17 years (1983–2000). This is consistent with the average groundwater velocity estimated for the GET E aquifers (1.6 ft/day) and supports NDMA transport by advective flow (Aerojet, 2000). Concentrations above 100 ng/L persist downgradient in a relatively uniform fashion for approximately 2000 ft from injection wells. These NDMA concentrations are close to the estimates for source water (250 ng/L) and indicate that degradation is not a significant process in this plume.

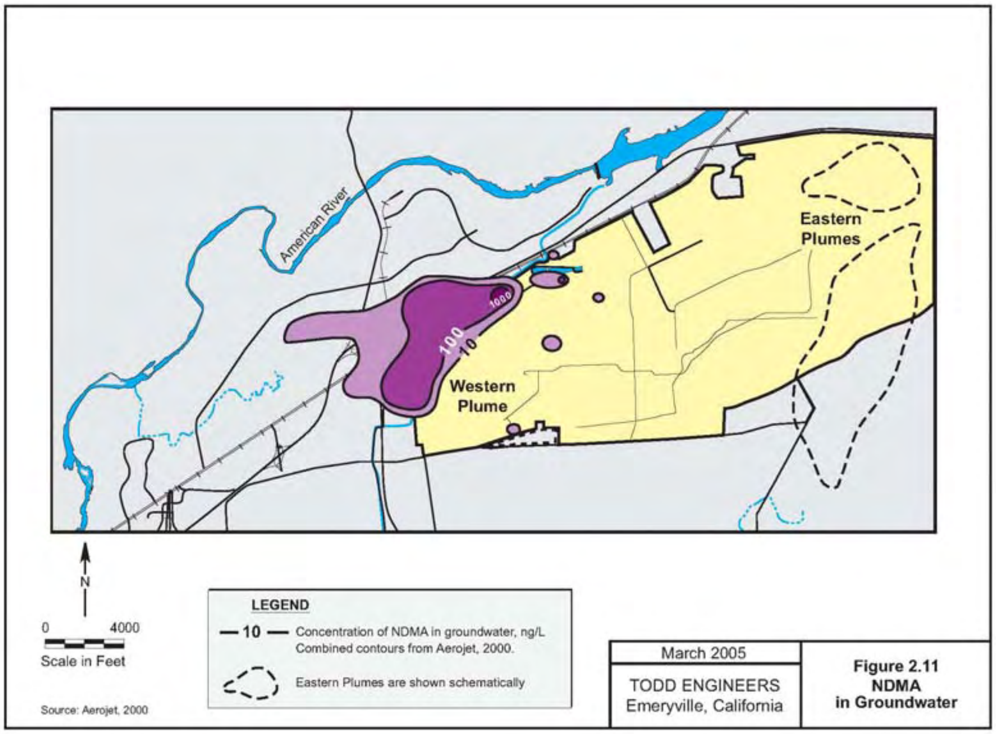


**Figure 2.11. NDMA in Groundwater, Rancho Cordova Site.**

Although the western plume seems wide, the effects of dispersion are not known. The width could be due to the release of NDMA into a bank of injection wells that create radial flow in most aquifer layers. The width could also be explained by NDMA releases from multiple source areas such as the GET wells and West Lake. The northern portion of the plume has migrated farther than the remaining plume; this “arm” may indicate aquifer heterogeneity or an older release from West Lake that was not captured by GET E extraction wells.

### 2.5.8 NDMA Fate and Transport Summary

*NDMA Detections*

- NDMA concentrations in source water released in most of the NDMA source areas are not readily available. NDMA concentrations in source water can be quantified on the western portion of the property, where a plume of NDMA originates from injection wells.
- Concentrations of injection water have been measured at 250 ng/L. The variability of concentrations over time is not known, but nearby groundwater extraction wells have consistently detected NDMA at similar concentrations since the beginning of injection, with an average concentration of 171 ng/L.
- Two main source areas on the eastern portion of the property have also impacted groundwater. Many wells in both areas detect NDMA at concentrations exceeding 10,000 ng/L. One plume appears to have migrated offsite. The other plume appears to have been contained by extraction wells.

*NDMA Fate and Transport in Groundwater at the Rancho Cordova Site*

- For all plumes, elevated concentrations persist for a substantial length of the plume, indicating that degradation is not a significant controlling factor in decreasing concentrations downgradient.
- For the western plume, concentrations in groundwater are similar to concentrations in the source water for more than 1000 ft downgradient, again indicating little or no degradation.
- All NDMA groundwater plumes are consistent with groundwater flow directions. The western plume is consistent with observed groundwater velocity estimates in the vicinity of the GET E wells, indicating that NDMA is not retarded with respect to groundwater flow.
- The width of the NDMA plumes cannot be used to analyze the effects of dispersion. For the eastern plumes, exact source areas have not been researched and extraction wells complicate the analysis. The western plume is the commingling of at least two source areas (West Lake and GET E injection wells). Source water was injected into several injection wells where radial flow is expected. An isolated “arm” of the plume indicates that the plume narrows were not commingled with other plumes.

## 2.6 MONTEBELLO FOREBAY RECHARGE PROJECT (MFRP)

### 2.6.1 Introduction

The Sanitation Districts of Los Angeles County (Sanitation Districts) operates three wastewater reclamation plants that provide recycled water for groundwater recharge at two spreading grounds in the Montebello Forebay, i.e., the Rio Hondo Spreading Grounds and the San Gabriel Spreading Grounds (Figures 2.2 and 2.12). The treatment plants include the WN, San Jose Creek, and Pomona Water Reclamation Plants (collectively, WRPs). The San Jose

Creek WRP includes two separate facilities, i.e., San Jose Creek East and San Jose Creek West. Figure 2.12 shows the locations of the WRPs and spreading grounds.

NDMA has been detected in WRP effluent, recharge water at the spreading grounds, and some nearby groundwater monitoring and production wells. Sanitation Districts has provided these data to support the analysis of NDMA fate and transport in groundwater. The Sanitation Districts is also conducting additional studies on the attenuation and dilution of NDMA between the WRP discharges and groundwater. This report documents the NDMA groundwater monitoring data.

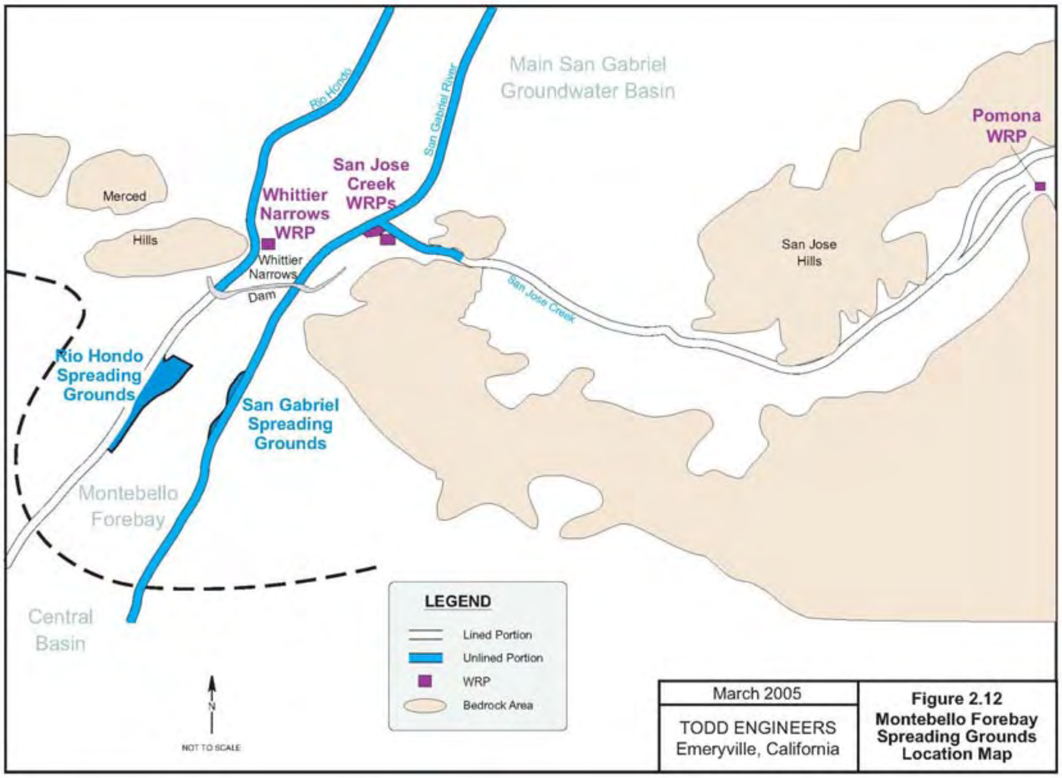


**Figure 2.12. Montebello Forebay Spreading Grounds Location Map.**

### 2.6.2 Project Description

The WRPs are located along the southern rim of the Main San Gabriel Groundwater Basin, while the spreading grounds are in the Montebello Forebay area of the Central Groundwater Basin (Figures 2.2 and 2.12). Recycled water is released at the WRPs into nearby surface water drainageways, including San Jose Creek, San Gabriel River, and Rio Hondo (Figure 2.12). Water flows along both lined and unlined portions of these drainageways to the spreading grounds. Some infiltration of recycled water along the unlined portions of these drainageways likely occurs. Recycled water is diverted from surface channels into the spreading grounds to allow infiltration into the unconsolidated alluvial sediments of the Montebello Forebay. Water recharged at the spreading basins also includes storm water and imported water.

The LARWQCB has issued Waste Discharge Requirements (WDRs) for the San Jose Creek and Pomona WRPs that establish NDMA effluent limits. To date, no effluent limits for NDMA have been established for the WN WRP. Table 2.3 summarizes these requirements.

**Table 2.3. Effluent Limits for NDMA for WN, San Jose Creek, and Pomona WRPs**

| WRP | Discharge limitation | | Interim limitation monthly avg (ng/L) | Notification level (ng/L) |
|---|---|---|---|---|
| | Daily avg (ng/L) | Monthly avg (ng/L) | | |
| WN | NE[1] | NE | NE | 10 |
| San Jose Creek East and West | 16,000 | 8100 | 20,000 | 10 |
| Pomona | 16,000 | 8100 | NE | 10 |

[1] NE, no effluent limit established.

The Sanitation Districts are required to comply with the interim effluent limit for the San Jose Creek WRPs until May 10, 2009. The WDRs for San Jose Creek and Pomona WRPs will be reevaluated on July 30, 2007, for possible modification of the final NDMA effluent limits. The Sanitation Districts has conducted and is planning to conduct a number of studies to assess the treatment and transport and fate of NDMA in the environment. For example, a UV disinfection pilot project is being conducted at the WN WRP to assess the use of UV disinfection to reduce levels of NDMA in wastewater. Other projects include the following: (1) source control/pollution prevention, (2) NDMA Formation Study, (3) filter backwash diversion, (4) optimization of chlorination chemical usage, (5) optimization of polymer usage, (6) NDMA attenuation and dilution studies, (7) study of NDMA photolysis at Long Beach WRP, and (8) various other collaborative studies, including this study.

The NDMA attenuation and dilution studies at the Montebello Forebay Recharge site are part of a multiyear project that includes testing of stream bed and vadose zone parameters, installation and testing of additional shallow monitoring wells, testing of additional production wells and surface water stations, and the development of a surface water/vadose zone/groundwater model to assess the attenuation and dilution of NDMA between the WRPs and groundwater beneath the spreading grounds and unlined portions of the streams. The NDMA attenuation and dilution studies are currently scheduled to be completed in February 2007. Another study currently being conducted at the Montebello Forebay is a tracer study commissioned by the Water Replenishment District of Southern California (WRD) to evaluate travel times between the spreading grounds and nearby production wells. That study was scheduled for completion by about May 2005.

The effluent limits for NDMA at the San Jose Creek and Pomona WRPs are above the California NL of 10 ng/L for NDMA in drinking water. An MCL, which is an enforceable standard for drinking water based on human health effects, has not been established for NDMA.

Water recharged in the MFRP is required to be a mix of reclaimed water, local storm water, and imported water. In accordance with LARWQCB, water reclamation requirements for the MFRP are as follows:

- The average quantity of reclaimed water in the basin recharge water (based on a running 3-year average) shall not exceed 60,000 acre-feet per year (AFY) or 50% of the total inflow into the basins for that year, whichever is less, and
- The maximum quantity of reclaimed water spread in any three-year period shall not exceed 150,000 AFY and 35% of the total inflow.

While these requirements have generally been met in the past, there are periods of time when storm water and imported water are unavailable and 100% of the water in the recharge basins is reclaimed water.

Imported water used for recharge water at the Rio Hondo and San Gabriel spreading grounds is predominantly untreated Colorado River water and State Water Project (SWP) water. On average (1961–1998), the makeup of the recharge water is approximately 30% reclaimed water, 35% local water, and 35% imported water. Of the total recycled water recharged at the basins, the largest volume comes from the San Jose WRP. Over the last 10 years (1992–2002), approximately 72% of the recycled water has come from the San Jose WRP, with approximately 22% from the WN WRP and 6% from the Pomona WRP. Thus, the water quality characteristics of the San Jose Creek WRP effluent have more effect on water quality in the recharge basins than do the other WRPs.

### 2.6.3 Hydrogeologic Setting

The Montebello Forebay is located in the northern area of the Central Basin on the Los Angeles Coastal Plain (Figure 2.2). The northern boundary of the basin is defined by consolidated sediments that crop out in the low-lying hills on both sides of WN, including the Puente Hills and Merced Hills. The Montebello Forebay connects with the San Gabriel Groundwater Basin at WN, where an erosional notch in the hills allows for surface and subsurface inflow.

Aquifers are composed of unconsolidated alluvial sediments of Recent to Early Pleistocene in age extending to depths of more than 1000 ft. Aquifers delineated beneath the forebay from shallow to deepest include the Gaspur, Gardena-Gage, Silverado, and Sunnyside aquifers (*Planned Utilization*, 1961). Aquifers are well interconnected and permeable sands and gravels occur on the ground surface. Aquitards exist in other portions of the Coastal Plain, but in the Montebello Forebay, sediments are coarser and allow surface recharge to percolate more deeply. As such, the Montebello Forebay is an important area of groundwater recharge for the Central Basin.

The predominant groundwater flow direction in the vicinity of the spreading grounds is to the southwest into the Central Basin. Regionally, groundwater flows west and south in portions of the forebay running as inflow through WN create a semiradial flow pattern (Figure 2.2).

### 2.6.4 Monitoring Data

Water quality monitoring is conducted by the Sanitation Districts and WRD at various points between the WRPs and groundwater beneath and around the spreading grounds as required under the WRP Monitoring and Reporting Program (MRP) and Montebello Forebay groundwater recharge MRP requirements. Monitoring is conducted at the WRP outfalls (effluent), at surface water stations upgradient and downgradient of the WRPs, at the Rio Hondo and San Gabriel recharge grounds intakes, at shallow groundwater monitoring wells adjacent to the recharge basins, and at deeper water supply production wells near the spreading grounds. While monitoring for many effluent constituents has been taking place for many years, NDMA testing began only relatively recently, in 2000. Figure 2.13 shows locations of monitoring and production wells near the spreading grounds.

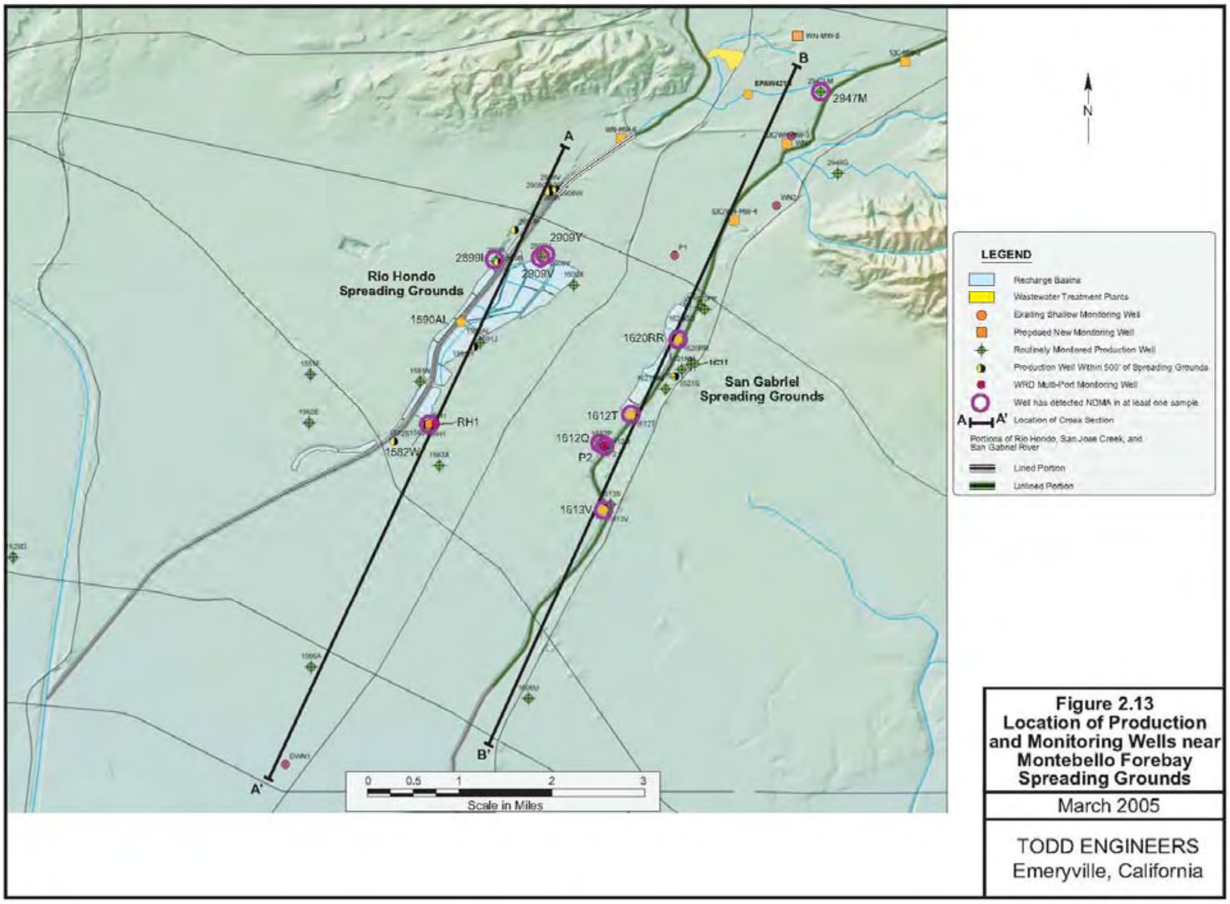


**Figure 2.13. Locations of Production and Monitoring Wells near Montebello Forebay Spreading Grounds.**

As part of the ongoing NDMA attenuation and dilution studies, additional surface water stations, shallow groundwater monitoring wells along unlined portions of the streams, production wells near the spreading grounds, and multiport wells near the spreading grounds will be monitored.

Water quality data are also collected for imported water by the Metropolitan Water District (MWD) and for storm water by the Los Angeles County Department of Public Works. Raw Colorado River water is monitored at Lake Mathews, and raw SWP water is monitored at Silverwood Dam, although surface water and imported water are not routinely tested for NDMA.

Table 2.4 identifies the time frame for which NDMA data are available for effluent, recharge water, shallow monitoring wells, multiport wells, and production wells. Figure 2.13 shows the locations of shallow monitoring wells, deeper water supply production wells, and multiport monitoring wells. The screened intervals and aquifers for each monitoring, multiport, and production well are listed in Table 2.5.

**Table 2.4. Sampling Station, Period, and Frequency at the MFRP[1]**

| Station | NDMA data | Frequency of NDMA sampling |
|---|---|---|
| **Effluent** | | |
| San Jose Creek East | July 00–March 04 | Monthly |
| San Jose Creek West | July 00–Feb 04 | Monthly |
| WN | July 00–March 04 | Monthly |
| Pomona | July 00–March 04 | Monthly |
| **Recharge basins** | | |
| Rio Hondo | April 00–March 01 | Quarterly |
| San Gabriel | April 00–April 01 | Quarterly |
| **Shallow wells near Rio Hondo Basins** | | |
| 2909Y | Apr 00–Feb 04 | Bimonthly |
| 1590AL | Apr 00–Feb 04 | Bimonthly |
| 1582W | Nov 99–Feb 04 | Bimonthly |
| Rio Hondo 1 (Zones 1–6) | Nov 99–June 01 | No regular monitoring |
| **Shallow wells near San Gabriel Basins** | | |
| 1620RR | April 00–Feb 04 | Bimonthly |
| 1612T | April 00–Feb 04 | Bimonthly |
| 1613V | April 00–Feb 04 | Bimonthly |
| Pico 1 (Zones 2–4) | July 01 | No regular monitoring |
| Pico 2 (Zones 1–6) | June 01 | No regular monitoring |
| Downgradient | | |
| Downey 1 | June 00–June 01 | No regular monitoring |
| **Deep production wells near Rio Hondo Spreading Grounds** | | |
| **Upgradient** | | |
| 2947LM | June 01–Dec 03 | Semiannual |
| 2908V | Dec 00–Dec 03 | Semiannual |

*Continues*

**Table 2.4.** ***Continued***

| Station | NDMA data | Frequency of NDMA sampling |
|---|---|---|
| **Near** | | |
| 2909V | Dec 00–Dec 03 | Semiannual |
| 2899I | Dec 00–Dec 03 | Semiannual |
| 1581N | June 01–Dec 03 | Semiannual |
| 1551F | June 01–Dec 03 | Semiannual |
| 1600X | June 01–Feb 03 | Semiannual |
| 1591H | Dec 00–Dec 03 | Semiannual |
| 1583X | June 00–Dec 03 | Semiannual |
| 1562E | June 00–Dec 03 | Semiannual |
| **Downgradient** | | |
| 1514A | June 01 | Semiannual |
| 1566A | June 01–Dec 03 | Semiannual |
| **Deep production wells near San Gabriel Spreading Grounds** | | |
| **Upgradient** | | |
| 2947LM | June 01–Dec 03 | Semiannual |
| 2948G | June 01–Dec 03 | Semiannual |
| **Near** | | |
| 1620GG | Dec 00–Dec 03 | Semiannual |
| 1620PP | Dec 00–Dec 03 | Semiannual |
| 1621T | Dec 00–Dec 01 | Semiannual |
| 1621MM | Dec 00–Dec 03 | Semiannual |
| 1621NN | June 03–June 04 | Semiannual |
| **Downgradient** | | |
| 1612Q | Dec 00–June 02 | Semiannual |
| 1606U | Dec 00–Dec 03 | Semiannual |
| 1566A | June 01–Dec 03 | Semiannual |
| 1612P | June 03–Dec 03 | Semiannual |
| **Imported water** | | |
| Colorado River | NT | No regular monitoring |
| SWP | 1999 | No regular monitoring |
| **Storm water** | | |
| S14 | NT | No regular monitoring |

[1] NT, not tested.

## Table 2.5. Construction Information for Shallow Monitoring, Multiport, and Deep Production Wells at the MFRP[1]

| Well | Aquifer | Screened interval (feet bgs) |
|---|---|---|
| **Shallow monitoring wells** | | |
| 1582W | Gaspur | 70–132 |
| 1590AL | Gaspur | 51–91 |
| 1612T | Gaspur | 60–80 |
| 1613V | Gaspur | 35–110 |
| 1620RR | Gaspur | 50–80 |
| 2909Y | Gaspur | 60–115 |
| **Multiport monitoring wells** | | |
| Downey 1-6 | Gaspur | 90–110 |
| Downey 1-5 | Exposition | 250–270 |
| Downey 1-4 | Hollydale/Jefferson | 370–390 |
| Downey 1-3 | Silverado | 580–600 |
| Downey 1-2 | Silverado | 940–960 |
| Downey 1-1 | Sunnyside | 1170–1190 |
| Pico 1-4 | Jefferson | 170–190 |
| Pico 1-3 | Silverado | 380–400 |
| Pico 1-2 | Silverado | 460–480 |
| Pico 2-6 | Gaspur | 100–120 |
| Pico 2-5 | Lynwood | 235–255 |
| Pico 2-4 | Silverado | 320–340 |
| Pico 2-3 | Sunnyside | 560–580 |
| Pico 2-2 | Sunnyside | 830–850 |
| Pico 2-1 | Sunnyside | 1180–1200 |
| Rio Hondo 1-6 | Gardena | 140–160 |
| Rio Hondo 1-5 | Lynwood | 280–300 |
| Rio Hondo 1-4 | Silverado | 430–450 |
| Rio Hondo 1-3 | Sunnyside | 710–730 |
| Rio Hondo 1-2 | Sunnyside | 910–930 |
| Rio Hondo 1-1 | Sunnyside | 1110–1130 |
| **Deep production wells** | | |
| 1514A | Lynwood | 500–600 |
| 1543J | Gage, Hollydale | 126–275 |
| 1551F | Gage, Hollydale, Lynwood | 142–405 |
| 1562E | Silverado | 422–556 |
| 1566A | Lynwood, Silverwood | 345–572 |
| 1581N | Lynwood, Silverwood | 230–624 |
| 1583X | Hollydale, Silverado | 235–422 |
| 1591H | Silverado, Sunnyside | 288–586 |
| 1600X | Silverado, Sunnyside | 294–456 |
| 1606U | Hollydale, Jefferson, Lynwood | 193–361 |
| 1612Q | Lynwood, Silverado | 242–446 |
| 1620GG | Silverado | 305–462 |
| 1620PP | Gardena, Jefferson, Lynwood, Silverado | 172–520 |
| 1621T | Gaspur, Jefferson, Lynwood, Silverado | 75–611 |
| 1621MM | Jefferson, Lynwood, Silverado, Sunnyside | 184–698 |
| 2899I | Gaspur, Gage, Lynwood, Silverado | 60–352 |
| 2908V | Sunnyside | 160–230 |
| 2909V | Lynwood, Silverado | 148–399 |
| 2947LM | Gardena, Jefferson, Lynwood, Silverado, Sunnyside | 180–800 |
| 2948G | Jefferson, Hollydale, Lynwood | 137–264 |

[1] bgs, below ground surface.

Groundwater beneath the spreading basins is shallow due to groundwater mounding, creating a thin vadose zone. The average depth to groundwater is approximately 18 ft beneath the San Gabriel Spreading Grounds and approximately 35 ft below the Rio Hondo Spreading Grounds. Due to the recharge operations and groundwater mounding, travel time between the spreading grounds and nearby shallow monitoring wells is very short, and it is likely that most of the water in shallow monitoring wells is composed of recharge water during periods of active recharge operations.

### 2.6.5 Tracer Studies

One tracer study has been completed, and a second study is currently under way at the Montebello Forebay. The first study was conducted between December 1999 and July 2000 by the Sanitation Districts and Lawrence Livermore National Laboratory (LLNL) at the Rio Hondo Spreading Grounds to determine recharge water travel times, mixing, and flow paths to the monitoring and production wells (Sanitation Districts Tracer Study). The second study is currently being conducted at both the Rio Hondo and San Gabriel Spreading Grounds by the WRD and University of California at Santa Barbara to evaluate travel times between the spreading grounds and nearby production wells and to collect scientific data on the movement of recharge water through multiple aquifer systems (WRD Tracer Study). Results of the WRD Tracer Study are expected in the next few months.

The Sanitation Districts’ Tracer Study data indicated that a portion of the recharge water moves very rapidly and reaches nearby shallow monitoring wells within one day. Tracer was detected at very low levels at wells deeper than 140 ft bgs, providing evidence of some vertical transport of the recharge water to zones deeper than 140 ft. Preliminary dilution calculations suggested that recharge water infiltrated upstream of the Rio Hondo Spreading Grounds may represent a larger percentage of water in well samples than does water from the spreading grounds, but the study concluded that additional work to further address this conclusion would be required.

Preliminary data available from the WRD Tracer Study indicate that tracer was detected in five of six shallow groundwater monitoring wells (monitored under the groundwater recharge MRP requirements) within 6 months; these wells include 1620RR, 1590AL, 1612T, 2909Y, and 1582W. Tracer was not detected in the two shallowest screened intervals of multiport well Pico 2 or Rio Hondo 1. Tracer was monitored in 17 production wells located within 500 ft of the spreading grounds and was detected in four production wells within 6 months. Two of these four wells (2899I and 2909V) are monitored for NDMA semiannually under the groundwater recharge MRP requirements.

### 2.6.6 NDMA in Recycled Water

The San Jose Creek East, San Jose Creek West, WN, and Pomona WRPs have tertiary treatment systems that consist of activated sludge secondary treatment followed by inert media filtration and disinfection with chloramines. In addition, as of June 2003, all WRPs were upgraded to include full nitrification and denitrification (NDN) treatment to reduce nitrogen compounds in wastewater. Effluent total suspended solids (SS) increased by over 200% when the NDN system was installed. To lower effluent total SS, polymers were added prior to clarification and disinfection. NDMA is generated as a byproduct of wastewater disinfection. In general, higher concentrations of NDMA were observed after the NDN upgrades because the polymers served as sources of NDMA precursors (Najm and Trussell, 2001; Mitch and Sedlak, 2004). As discussed above, the Sanitation Districts has and is currently conducting several programs to identify methods for lowering NDMA concentrations in their final effluents.

NDMA sampling results for treated effluent from the San Jose Creek, WN, and Pomona WRPs are plotted in Figure 2.14. NDMA is tested on a monthly basis in effluent discharged from the WRPs. As shown in the figure, NDMA is consistently detected in treated effluent from all four WRPs. However, all samples have been below the 20,000-ng/L interim effluent limit.

NDMA concentrations in WRP effluent are highly variable over time within each WRP as well as from plant to plant. This variability is demonstrated by the range of concentrations, averages, and standard deviations as summarized in Table 2.6.

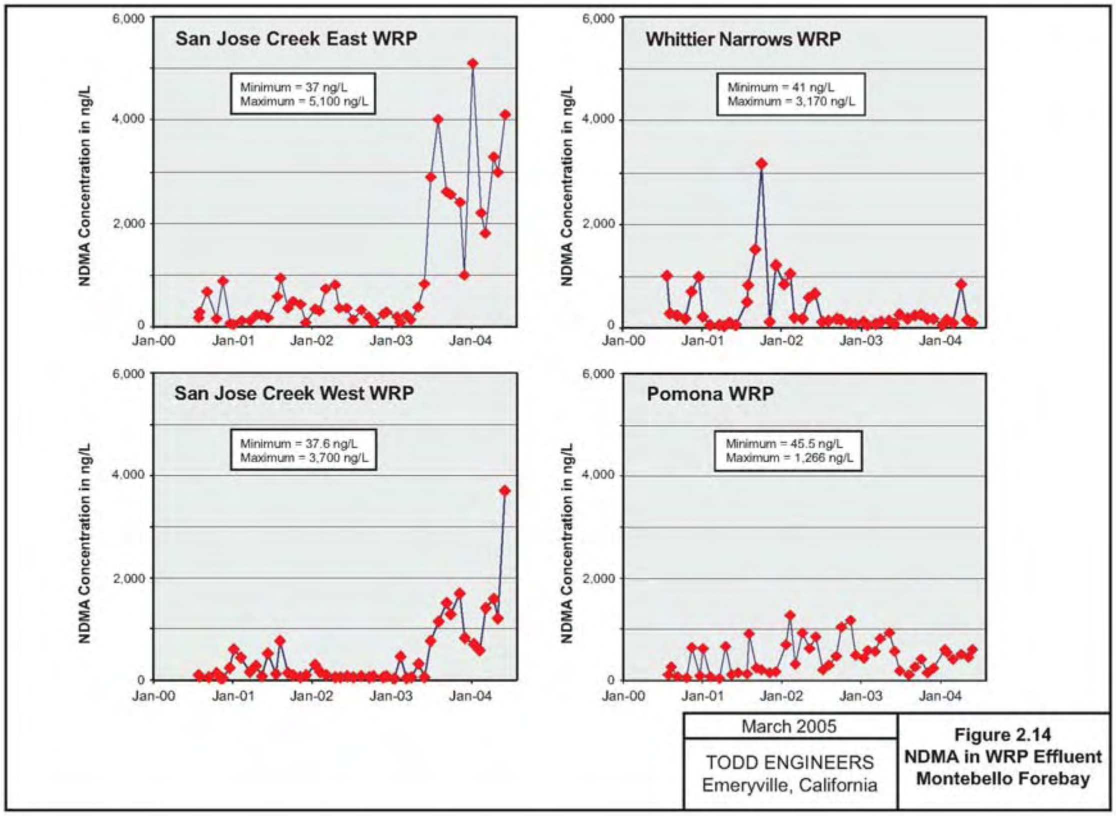


**Figure 2.14. NDMA in WRP Effluent, Montebello Forebay.**

**Table 2.6. NDMA Concentrations in Effluent at the MFRP**

| WRP | Minimum NDMA concn (ng/L) | Maximum NDMA concn (ng/L) | Avg NDMA concn (ng/L) | SD |
|---|---|---|---|---|
| San Jose Creek West | 37.6 | 3700 | 438 | 658 |
| San Jose Creek East | 37 | 5100 | 978 | 1270 |
| WN | 41 | 3170 | 396 | 545 |
| Pomona | 45.5 | 1270 | 450 | 315 |

The San Jose Creek East WRP has had the highest detected concentration of NDMA at 5100 ng/L (Figure 2.14). Approximately 40% of the effluent flow at the San Jose Creek East WRP received NDN treatment starting in August 2000, with 100% receiving NDN treatment by June 13, 2003. NDMA concentrations in San Jose Creek East effluent showed a significant increase after implementation of NDN in June 2003.

The highest NDMA concentration detected at the San Jose Creek West WRP has been 3700 ng/L (Figure 2.14). NDN treatment was in full operation at the San Jose Creek West WRP as of June 13, 2003. Similar to the trend observed at the San Jose Creek East WRP, NDMA concentrations increased after implementation of the NDN in June 2003 at the San Jose Creek West WRP.

The highest NDMA concentration in the Whittier WRP effluent was detected in October 2001 at 3170 ng/L (Figure 2.14). Pilot testing of NDN treatment at the WN WRP was completed in January 2001, which is when full operation of the NDN treatment system became operational. NDMA concentrations increased from mid-2001 through mid-2002 and have typically been below 400 ng/L since mid-2002.

The highest NDMA concentration in Pomona WRP effluent has been 1270 ng/L (Figure 2.14). Full implementation of NDN treatment began at the Pomona WRP on June 13, 2003. Unlike the other WRPs, NDMA concentrations in Pomona WRP effluent did not show an increase after implementation of the NDN treatment. NDMA concentrations in Pomona WRP effluent are usually below 1000 ng/L.

Although NDMA concentrations in WRP effluent consistently meet regulatory requirements, including interim, daily, and monthly discharge limits, NDMA is consistently detected in WRP effluent and has been highly variable over time. Data indicate that NDMA effluent concentrations increased after implementation of NDN at the San Jose Creek WRPs, showed a temporary increase at the WN WRP, and did not increase at the Pomona WRP. However, these concentrations are not representative of recharge water at the spreading basins, as discussed in more detail below.

### 2.6.7 NDMA in Recharge Water

Since 2000, 13 recharge water samples have been collected at the intakes of the Rio Hondo Spreading Grounds (six samples) and San Gabriel Spreading Grounds (seven samples) and analyzed for NDMA. Data are presented in Table 2.7 below and plotted over time in Figure 2.15.

**Table 2.7. NDMA Concentrations in Recharge Water at the MFRP[1]**

| Sampling date | NDMA in recharge water (ng/L) | |
|---|---|---|
| | Rio Hondo | San Gabriel |
| April 2000 | 11 | 13 |
| June 2000 | 8.8 | 18 |
| October 2000 | NS | 392 |
| December 2000 | 9.4 | 34 |
| March/April 2001 | 17 | 21 |
| February/March 2004 | 9.4 | 48 |
| June 2004 | 290 | NS |
| October 2004 | NS | 110 |

[1] NS, no sample collected.

Recharge water is generally sampled on a quarterly basis in accordance with groundwater recharge MRP requirements; however, samples were not collected between approximately April 2001 and February 2004, perhaps because of dry conditions. The spreading grounds can be dry for long periods of time due to permit limitations. As a result, recharge water data are not available during the period when NDMA concentrations were at their highest following NDN implementation at the San Jose Creek WRP.

NDMA has been detected in all recharge water samples, but as shown in Table 2.7 above, concentrations are highly variable. Concentrations have ranged from 8.8 to 392 ng/L. The highest NDMA concentration in recharge water was detected at the intake for the San Gabriel Spreading Grounds (392 ng/L). The highest NDMA concentration in Rio Hondo Spreading Grounds recharge water has been 290 ng/L.

NDMA concentrations in recharge water are generally an order of magnitude lower than in WRP effluent. The likely cause of the lower concentrations is the photolysis that occurs along the surface water flow path to the spreading basins. This flow path allows for exposure to sunlight, which is known to break down NDMA (Mitch et al., 2003a). These concentrations may also be diluted with water from other sources such as storm water or imported water flowing into the spreading grounds with the effluent.

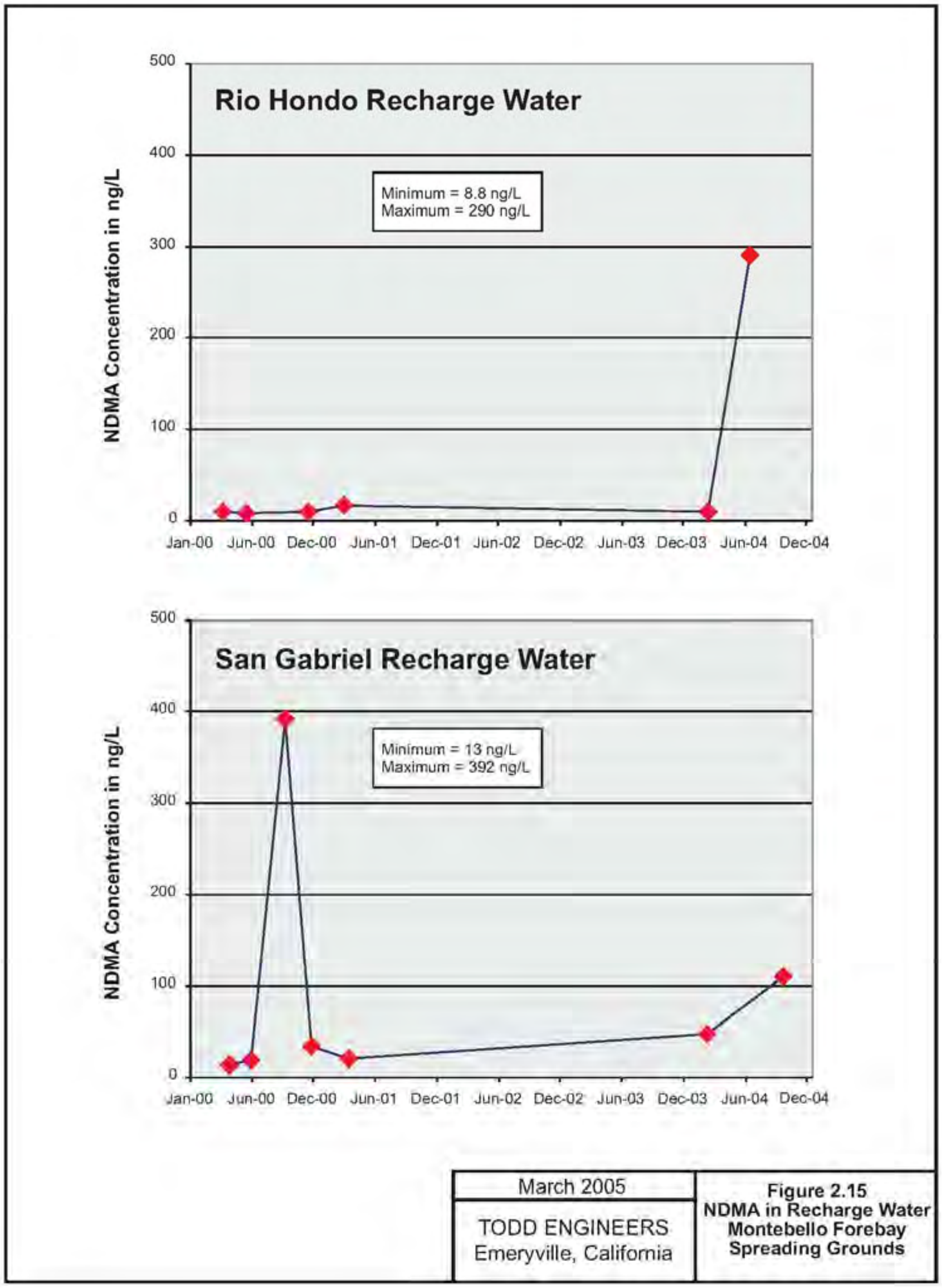


**Figure 2.15. NDMA in Recharge Water, Montebello Forebay Spreading Grounds.**

### 2.6.8 NDMA in Groundwater

NDMA has been tested in shallow monitoring wells, deep production wells, and multiport monitoring wells in the vicinity of the spreading grounds since about 2000. Wells where NDMA has been detected in at least one sample are circled in Figure 2.13. With one exception (i.e., upgradient Well 1947M), all of the NDMA detections have been near or in the spreading grounds. Concentrations are generally higher in shallow groundwater, but NDMA has been detected in several production wells. NDMA persists downgradient at least 1 mi as evidenced by detections in a shallow monitoring well, but concentrations have not exceeded 7 ng/L. Only a few wells further downgradient are monitored, but NDMA has not been detected in samples from those wells. A more detailed discussion of the NDMA testing and detection is provided below.

### 2.6.9 NDMA in Shallow Groundwater Monitoring Wells

NDMA testing has been conducted in the six shallow groundwater wells as part of the groundwater recharge MRP requirements. Well locations are shown in Figure 2.13. The wells are screened in the shallowest water-bearing zone beneath the spreading basins; screened intervals for specific wells are provided in Table 2.5. NDMA test results are summarized in the following table and discussed below.

**Table 2.8. NDMA Concentrations in Shallow Monitoring Wells – MFRP[1]**

| Well | Spreading ground location | | No. of NDMA samples | No. of NDMA detections | Minimum NDMA concn (ng/L) | Maximum NDMA concn (ng/L) |
|---|---|---|---|---|---|---|
| 2909Y | Upgradient | RHSG | 27 | 9 | <2 | 9.3 |
| 1590AL | Central | RHSG | 27 | 0 | <2 | <2 |
| 1582W | Downgradient | RHSG | 26 | 2 | <2 | 2.5 |
| 1620RR | Central | SGSG | 26 | 13 | <2 | 460 |
| 1612T | Downgradient | SGSG | 21 | 6 | <2 | 170 |
| 1613V | Downgradient | SGSG | 27 | 6 | <2 | 6.9 |

[1] RHSG, Rio Hondo Spreading Grounds;
SGSG, San Gabriel Spreading Grounds.

NDMA is usually not detected or is detected at concentrations below 10 ng/L in the shallow monitoring wells near both recharge basins. NDMA concentrations near the Rio Hondo Spreading Grounds are consistently below 10 ng/L, the action level for drinking water. The highest concentrations near the Rio Hondo Spreading Grounds are detected in Well 2909Y, located on the upgradient edge of the spreading grounds, at 9.3 ng/L (Figure 2.13). This finding is consistent with the Sanitation Districts Tracer Study, which found significant contributions of recycled water upstream of the spreading grounds.

Two shallow wells near the San Gabriel River Spreading Grounds (1620RR and 1612T) have contained relatively high NDMA concentrations, although detections have been sporadic. Wells 1620RR and 1612T detected the highest concentrations of 460 and 170 ng/L, respectively, in October 2003 following implementation of the NDN treatment and the associated increase in NDMA in effluent. Well 1613V, located about 1 mi downstream of the San Gabriel Spreading Grounds, has also contained detectable concentrations of NDMA but at lower concentrations (up to 6.9 ng/L). These detections indicate that NDMA is present in downgradient groundwater up to 1 mi from the spreading grounds but that concentrations are much lower than those detected near the spreading grounds.

### 2.6.10 NDMA in Multiport Monitoring Wells

The WRD monitors several multiport monitoring wells located near the Rio Hondo and San Gabriel spreading grounds, including Pico 1, Rio Hondo 1, Pico 2, and Downey 1. These wells have multiple screened intervals and are capable of testing water quality at different depths in the same well. Wells have four to six sampling ports and are screened in various aquifers from 90 to 1200 ft deep. The screened intervals of the well ports are listed in Table 2.5, and well locations are shown in Figure 2.13 (well names are abbreviated P1, RH1, P2, and DWN1).

Pico 1 and Pico 2 are located upgradient and downgradient of the San Gabriel Spreading Grounds, respectively. Rio Hondo 1 is located at the downgradient edge of the main Rio Hondo Spreading Grounds near shallow monitoring well 1582W. Downey 1 is located more than 2½ mi downgradient of both the San Gabriel and Rio Hondo spreading grounds (Figure 2.13).

Only a few sampling events for NDMA have been conducted in these wells. Most of these samples were analyzed in 2000 and 2001; wells were sampled from one to four times. Only one port in one well (Port 6 in Pico 2) contained detectable concentrations of NDMA (2.6 ng/L). This port is the shallowest screen at a depth of 100 to 120 ft. As shown in Figure 2.13, Pico 2 is located just downgradient of the San Gabriel Spreading Grounds and about a third of a mile downgradient of shallow monitoring well 1612T, which has also contained NDMA in groundwater at concentrations up to 170 ng/L.

The detection suggests that NDMA persists in shallow groundwater downgradient. It is difficult to make conclusions about the rate of concentration decrease downgradient, given that Pico 2 was sampled only once and the sampling occurred several years before the higher concentrations were detected in upgradient well 1612T.

### 2.6.11 NDMA in Production Wells

NDMA data are available for 21 production wells in the vicinity of the spreading grounds. In general, production wells with deeper screens are monitored semiannually. The locations of the deeper production wells relative to the basins are shown in Figure 2.13, and the screen intervals are provided in Table 2.5.

Of the 21 wells tested, NDMA has been detected in only four wells, each in only one sampling event. These detections have ranged in concentration from 2.8 to 4.4 ng/L. NDMA has been detected in two production wells (2909V and 2899I) on one occasion each near the Rio Hondo Spreading Grounds. These wells are located on the upgradient side of the Rio Hondo Spreading Grounds near shallow monitoring well 2909Y. The nearby shallow monitoring well 2909Y contained the highest concentrations of NDMA detected in shallow wells near the Rio Hondo Spreading Grounds. Both of the Rio Hondo production wells, 2899I and 2909V, were found to have tracer travel times of less than 6 months in the WRD Tracer Study, indicating the wells are receiving recharge water from the spreading grounds.

NDMA has also been detected once in upgradient production well 2947M at 3.2 ng/L (Figure 2.13). This well is located more than 2½ mi upgradient of the San Gabriel Spreading Grounds near the San Gabriel River. It is difficult to interpret the source of NDMA in this well based on only one detection. The source could be reclaimed water that has percolated to underlying groundwater through unlined portions of the San Gabriel River. It is also possible that the source is associated with upgradient NDMA sources in the San Gabriel Basin or is the result of a sampling QA/QC problem. NDMA has also been detected in one production well downgradient of the San Gabriel Spreading Grounds, Well 1612Q. This well is located near multiport well Pico 2, where NDMA was also detected (Figure 2.13).

In general, the production well data indicate that NDMA is usually not detected in pumping wells, but when detected, concentrations are lower than those observed in shallow monitoring wells. This is expected, given the longer and deeper screens that allow for mixing of recharge water and other groundwater in the well sample. Pumping also creates vertical gradients, dispersing the recharge water and NDMA throughout the thick aquifers and decreasing NDMA concentrations.

Figures 2.16 and 2.17 are cross sections through the Rio Hondo and San Gabriel spreading grounds, respectively, and illustrate the geometry of the monitoring points and NDMA detections. Cross section locations are shown in Figure 2.13. The cross sections provide some information on the lateral and vertical distribution of NDMA in the vicinity of the spreading basins. The highest NDMA detection in each well along with the screened interval(s) is annotated on the cross sections.

Figure 2.16 illustrates NDMA detections on the upstream edge of the Rio Hondo Spreading Grounds in two production wells (2909V and 2899I) and two shallow monitoring wells (2909Y and 1582W). Four additional production wells (1600X, 1591H, 1581N, and 1583X) and two additional monitoring wells (1590AL and Rio Hondo 1) have not contained detectable concentrations of NDMA, even though they are located within or very near the spreading grounds and have screens that overlap depths where other wells have detected NDMA.

Figure 2.17 illustrates NDMA detections upgradient and downgradient of the San Gabriel Spreading Grounds. The upgradient production well (2947LM) has contained detectable concentrations of NDMA, once at a concentration of 3.2 ng/L (shown on the left side of the section). The source of this NDMA is unknown but is judged to be too far upgradient to have been impacted by recharge water at the spreading grounds. NDMA concentrations could be percolating from the surface or originating upgradient. NDMA has been detected in all three shallow monitoring wells (1620RR, 1612T, and 1613V), one production well (1612Q), and the shallow port in multiport well Pico 2. NDMA impacts appear to be in shallow groundwater.

### 2.6.12 Other Sources of NDMA

Water from other sources is also recharged at the Rio Hondo and San Gabriel spreading grounds. These sources have limited NDMA data. For example, storm water samples have not been analyzed for NDMA.

Until recently, imported water had been tested only once for NDMA, a 1999 sample collected at Silverwood Lake (SWP water) by MWD. NDMA was not detected at greater than the detection level of 2 ng/L in that sample. In December 2004, the Sanitation Districts collected

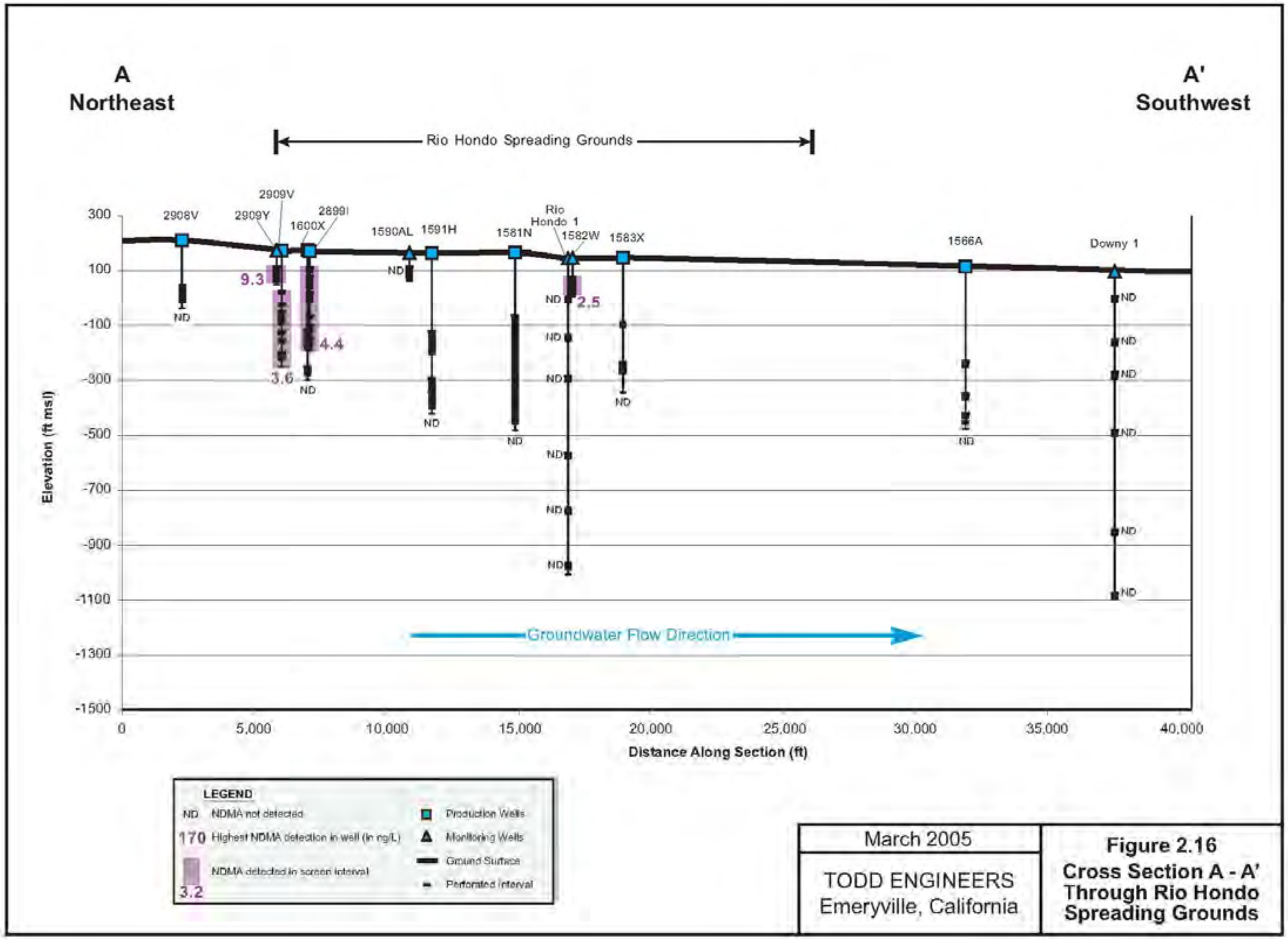


**Figure 2.16. Cross Section A-A’ through Rio Hondo Spreading Grounds.**

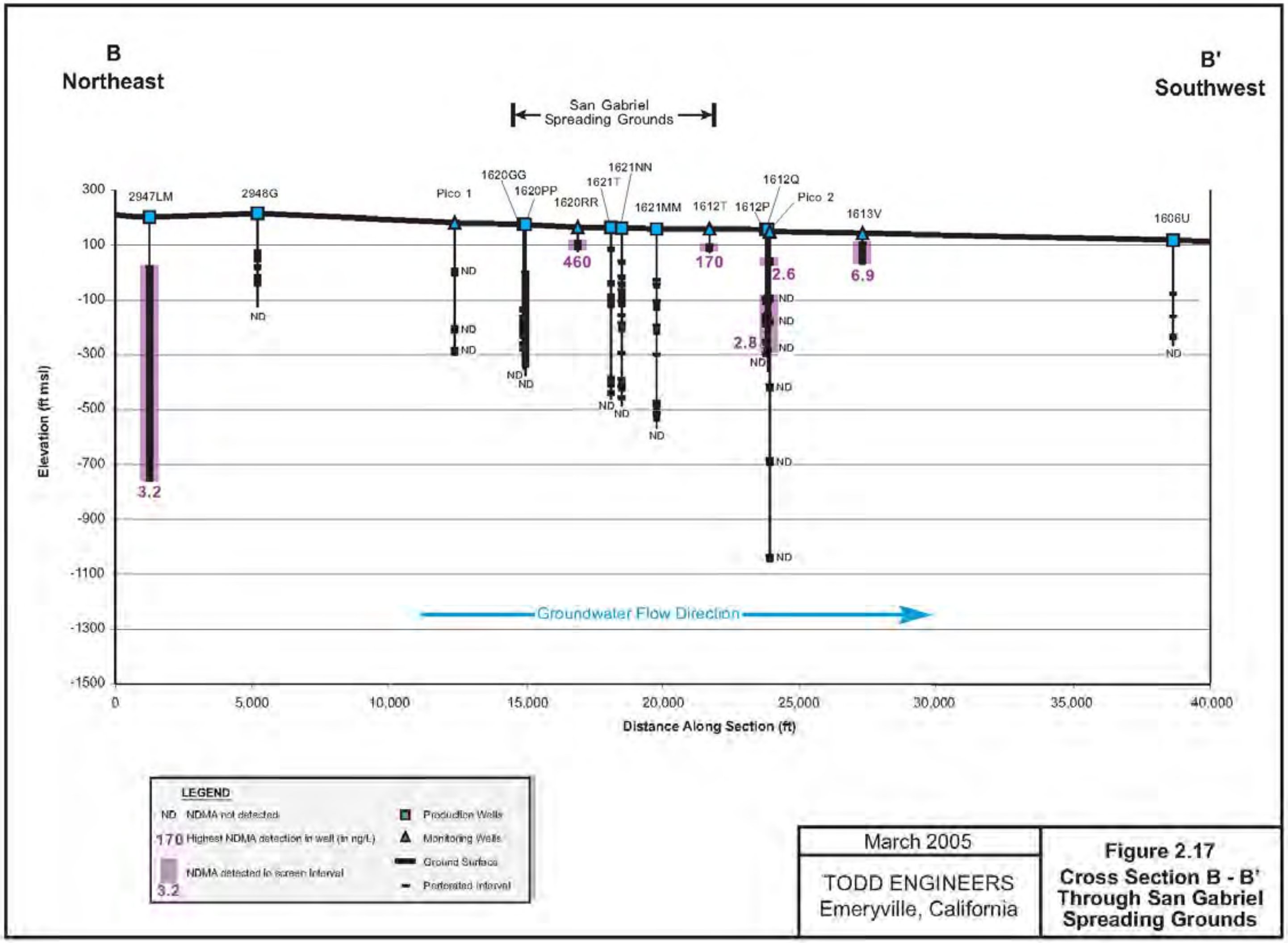


**Figure 2.17. Cross Section B-B' through San Gabriel Spreading Grounds.**

a sample of imported water where the water enters the San Gabriel Spreading Grounds. The imported water sample had an NDMA concentration of 4.8 ng/L. The result indicates that imported water may also be a source of NDMA in groundwater in the recharge water.

In addition, NDMA has been detected in USEPA monitoring wells installed for the San Gabriel Basin Superfund investigation upgradient of any WRP discharge in the WN area. These detections indicate that other sources of NDMA may be contributing to groundwater contamination in the vicinity of WN.

### 2.6.13 NDMA Fate and Transport Summary

*NDMA Detections*

- NDMA data for effluent, recharge water, and groundwater samples are generally available beginning in 2000, when NDMA monitoring began.
- NDMA is consistently detected in effluent from each of the project WRPs at concentrations ranging from 37 ng/L to 5100 ng/L, with an average concentration of 566 ng/L for all plants. NDMA concentrations in WRP effluent are variable from plant to plant and over time.
- Since June 2003, NDMA concentrations in effluent at the San Jose Creek WRPs have risen significantly due to the implementation of NDN treatment. Prior to June 2003, NDMA concentrations averaged 319 and 169 ng/L at the San Jose Creek East and West WRPs, respectively. After June 2003, NDMA concentrations averaged 2750 and 1100 ng/L at the East and West WRPs, respectively.
- NDMA is consistently detected in water that is diverted into the spreading grounds (recharge water), although data are limited. Concentrations are significantly lower and range from 8.8 to 392 ng/L, a range generally applicable to both spreading grounds.
- Recent increases in NDMA concentrations in recharge water at the San Gabriel Spreading Grounds are consistent with increasing NDMA concentrations in effluent from the San Jose Creek WRPs.
- NDMA has been detected in at least one groundwater sample from five shallow monitoring wells, one multiport monitoring well (shallow port only), and four production wells in the vicinity of the spreading grounds.
- NDMA has been detected in five of the six shallow monitoring wells around both spreading grounds. Detections are sporadic and generally occur below 10 ng/L, although one well in the central portion of the San Gabriel Spreading Grounds (Well 1620RR) detected NDMA at a concentration of 460 ng/L in one sampling event. This detection occurred just after concentrations in the San Jose Creek WRPs increased due to NDN treatment. However, subsequent NDMA detections in the well have been at least an order of magnitude lower, and recent samples have not detected NDMA.
- NDMA has been detected downgradient of the San Gabriel Spreading Grounds in a shallow monitoring well as far as 1 mi. Although additional downgradient monitoring points are limited, data indicate that NDMA is not present above detection levels further downgradient.
- NDMA has been analyzed in several samples from multiple depths in four multiport monitoring wells. Only one port in one well (Port 6 in Pico 2) has detected NDMA. The NDMA concentration was 2.6 ng/L and was detected in the well’s shallowest screen at a depth of 100 to 120 ft. The well is 2,300 ft downgradient from the San Gabriel Spreading Grounds.

- NDMA data are available from 21 production wells in the vicinity of the spreading grounds. Of the 21 wells, only four have detectable concentrations of NDMA, each in only one sampling event. NDMA concentrations ranged from 2.8 to 4.4 ng/L.
- Two production wells, 2909V and 2899I, are located on the upgradient edge of the Rio Hondo Spreading Grounds, and NDMA has been detected at 3.6 and 4.4 ng/L, respectively. One production well downgradient of the San Gabriel Spreading Grounds, Well 1612Q, contained detectable concentrations of NDMA at 2.8 ng/L. One production well, 2947M, contained detectable concentrations of NDMA more than 1 mi upgradient of the spreading grounds. This detection may be effluent that has infiltrated through the San Gabriel River channel into underlying groundwater or from an upgradient source of NDMA.
- NDMA has recently been detected in a sample of imported water (tested upstream where it enters the San Gabriel Basin) that is also recharged at the spreading grounds. NDMA was detected at a concentration of 4.8 ng/L.

*NDMA Fate and Transport in the MFRP*

- Two conditions may be responsible for the low NDMA concentrations in recharge water. First, degradation of NDMA by photolysis is likely occurring, as effluent is exposed to sunlight during surface water flow from the WRPs to the spreading grounds. Second, effluent NDMA concentrations are diluted when storm water and imported water are diverted into the spreading grounds.
- Data indicate that NDMA concentrations being recharged into the groundwater basin are too low and sporadic to track the fate and transport with certainty.
- Natural downward vertical gradients in this regional recharge area, coupled with enhanced vertical gradients from deep production wells, spread the recharge water vertically in the aquifer, mixing recharge water with native groundwater and decreasing NDMA concentrations.
- Dispersion in the aquifer and mixing of recharge water with local groundwater in well samples are likely the mechanisms responsible for decreasing NDMA concentrations downgradient and the lack of NDMA detections in some downgradient wells.
- Conclusions on fate and transport of NDMA in groundwater are limited by sparse NDMA data in recharge water, unknown volumes and NDMA concentrations in storm water and imported water recharged at the spreading grounds, and other factors.

## 2.7 TALBERT BARRIER PROJECT

### 2.7.1 Introduction

The Talbert Barrier consists of a line of injection wells along coastal Orange County installed to prevent seawater intrusion into drinking-water aquifers of the Coastal Plain Groundwater Basin (Figure 2.2). Since October 1976, treated wastewater from the Water Factory 21 treatment plant has been blended with groundwater and injected into barrier wells. NDMA was first analyzed and detected in treated wastewater and injection water in January 2000, likely resulting from chlorination. Since chlorination has always been a component of the treatment process at Water Factory 21, it is assumed that water containing NDMA has been injected into the groundwater basin over the last 28 years. In January 2000, Orange County Water District (OCWD), the operator of Water Factory 21, initiated an NDMA monitoring program including injection water, monitoring wells, and water supply wells in the vicinity and downgradient of the barrier. OCWD provided these data in support of this analysis of the fate and transport of NDMA in groundwater.

### 2.7.2 Available Data

Available data related to the Talbert Barrier site were provided by OCWD, including a combination of engineering reports, special study reports, water level maps, and several electronic databases. Electronic data included concentrations of NDMA, 1,4-dioxane, and selected inorganic constituents in injection water and groundwater. NDMA data were available from 2000, and inorganic data date back to the early 1990s. OCWD also provided three location maps in electronic format showing barrier wells, production wells, and monitoring wells within an approximately 2-mi-long radius away from the barrier.

### 2.7.3 Hydrogeologic Setting

The Orange County Coastal Plain Groundwater Basin overlies the lower Santa Ana River watershed along the coast of northwestern Orange County. The basin is bounded by the Pacific Ocean on the west and by a topographic divide at the Los Angeles County-Orange County line on the north (Figure 2.2). Bedrock hills line the basin on the east and south.

The groundwater basin is a structural depression created by the Newport-Inglewood fault zone where a thick accumulation of sediments has been deposited. Sediments include both marine and continental deposits of Pliocene to Recent age. Aquifers consist of permeable sands interbedded with fine-grain deposits that increase toward the coast. These permeable deposits result in high well yields, typically 2000 to 3000 gpm (*Coastal Plain*, 2004). Groundwater production on the Coastal Plain has reversed regional westerly gradients, allowing for seawater intrusion problems that date back to the 1930s.

Various aquifer nomenclatures exist in the literature. In the Department of Water Resources (DWR) Groundwater Bulletin 118, aquifers are divided into an Upper Aquifer, Middle Aquifer, and Lower Aquifer Systems. OCWD developed this nomenclature for construction of a basin-wide numerical model. However, more detailed nomenclature referring to specific sand layers is still in use, especially in reference to the four upper aquifers in the basin: Talbert, Alpha, Beta, and Lambda aquifers. These are the four main aquifers that have been delineated beneath the Talbert Barrier and the aquifers into which blend water is injected.

Following deposition of the Alpha, Beta, and Lambda aquifers, the Santa Ana River eroded portions of these geologic units between the Huntington Mesa and the Newport Mesa (Figure 2.18). Permeable fluvial sands of the Talbert Aquifer were deposited on the erosional surface. The Talbert sands provided a migration pathway, referred to as the Talbert Gap, for seawater intrusion into the basin. Seawater intrusion has been hydraulically controlled since 1976 by injection into approximately 41 injection wells. This east-west line of injection wells, referred to as the Talbert Barrier, is located approximately 3.5 mi inland between Huntington and Newport mesas (Figure 2.18).

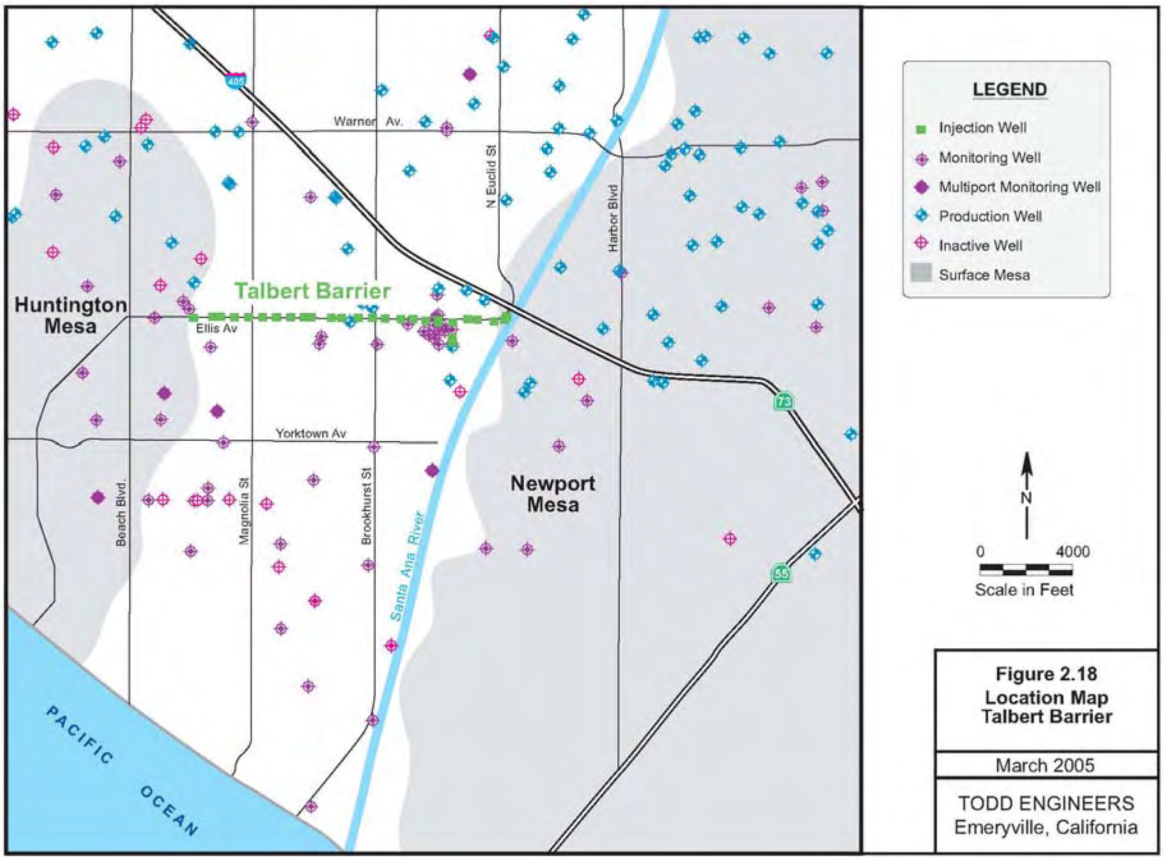


**Figure 2.18. Location Map, Talbert Barrier.**

Injection water raises water levels in the aquifers, creating radial flow away from the barrier. Estimates of groundwater flow around the barrier indicate that about 50% of the injection water flows inland to replenish the groundwater basin. Figure 2.19 shows the piezometric surface map for the Lambda Aquifer prepared by OCWD for September 2000. As shown by the contours and flow arrows in Figure 2.19, water injected into the Lambda Aquifer creates mounding near the injection wells and flows away from the barrier, especially inland. Groundwater production in the Lanbda Aquifer has created pumping depressions that encourage the inland flow (note the pumping depression identified by the water levels below –100 msl ft in the northeast portion of Figure 2.19). General flow conditions in the Lambda Aquifer are reflected in the other aquifers. Differences in piezometric surfaces in the Coastal Plain Basin aquifers are caused by differences in groundwater production and in the distance that seawater has intruded.

## 2.7.4 Barrier Operation

In October 1976, OCWD began blending and injecting recycled water from its Water Factory 21 treatment plant into the Talbert Barrier. Product water from Water Factory 21 combined effluent from two different treatment processes, activated carbon treatment (AWT) and reverse osmosis treatment (RO). From 1976 through 2001, the average amount of blended water injected into Talbert Barrier was $7.6 \times 10^6$ gal per day (mgd) (8524 AFY). On average, blend water was composed of 54% product water (both AWT and RO) and 46% groundwater. Since 2001, water from the cities of Fountain Valley and Huntington Beach has also been used to blend with Factory 21 effluent (product water) and deep well water prior to injection.

Barrier wells consist of 23 multiport injection wells and 18 single-zone injection wells screened in the four main shallow aquifers susceptible to seawater intrusion (Talbert, Alpha, Beta, and Lambda aquifers). These 41 wells are installed approximately 600 ft apart (Figure 2.18).

### 2.7.5 NDMA in Blend Water

NDMA was analyzed in 169 samples of injection water from January 28, 2000, through April 7, 2004. During this time, injection water was composed of various mixtures of recycled water, deep well groundwater, and water from the cities of Huntington Beach and Fountain Valley. Figure 2.20 shows a graph of NDMA concentrations in injection water that range from 310 ng/L to <2 ng/L and average 17 ng/L (standard deviation, 39). As shown on the graph, NDMA concentrations were highest from January 2000 to June 2000, when detections averaged 117 ng/L. From January 2000 through March 2001, NDMA concentrations averaged 65 ng/L. Average NDMA concentrations after March 2001 decreased significantly to 5 ng/L.

The sharp decrease in 2001 corresponded to the installation of UV treatment by OCWD to remove NDMA from recycled water. As a result, data for only 1 year (2000) are available to characterize NDMA concentrations that have been present in source water historically and compare with NDMA concentrations in groundwater. Prior to 2000, concentrations of NDMA in source water are unknown.

A review of other inorganic constituents in blend water indicates that the water chemistry of the blend water has not been stable over time. Figure 2.21 illustrates this variability with a plot of chloride and NDMA concentrations in injection water from 1994 to 2004. Over that 10-year period, chloride concentrations have ranged from <10 mg/L to >90 mg/L. Chloride concentrations were relatively high from July 1999 to July 2000 and were consistently low from July 2000 to March 2001. The decrease in chloride in 2000 is paralleled in NDMA (also plotted in Figure 2.21). Changes in chloride concentrations over time were determined to relate to changes in the amounts of the various source waters that are used for blending, as examined in more detail below.

Figure 2.22 shows a trilinear diagram of blend water chemistry that illustrates these changes. Similar water chemistry data will plot in clusters on the trilinear diagram. An examination of Figure 2.22 shows that samples with similar water chemistry can be grouped according to the time period in which injection water was analyzed. Clusters of similar samples are circled for emphasis.

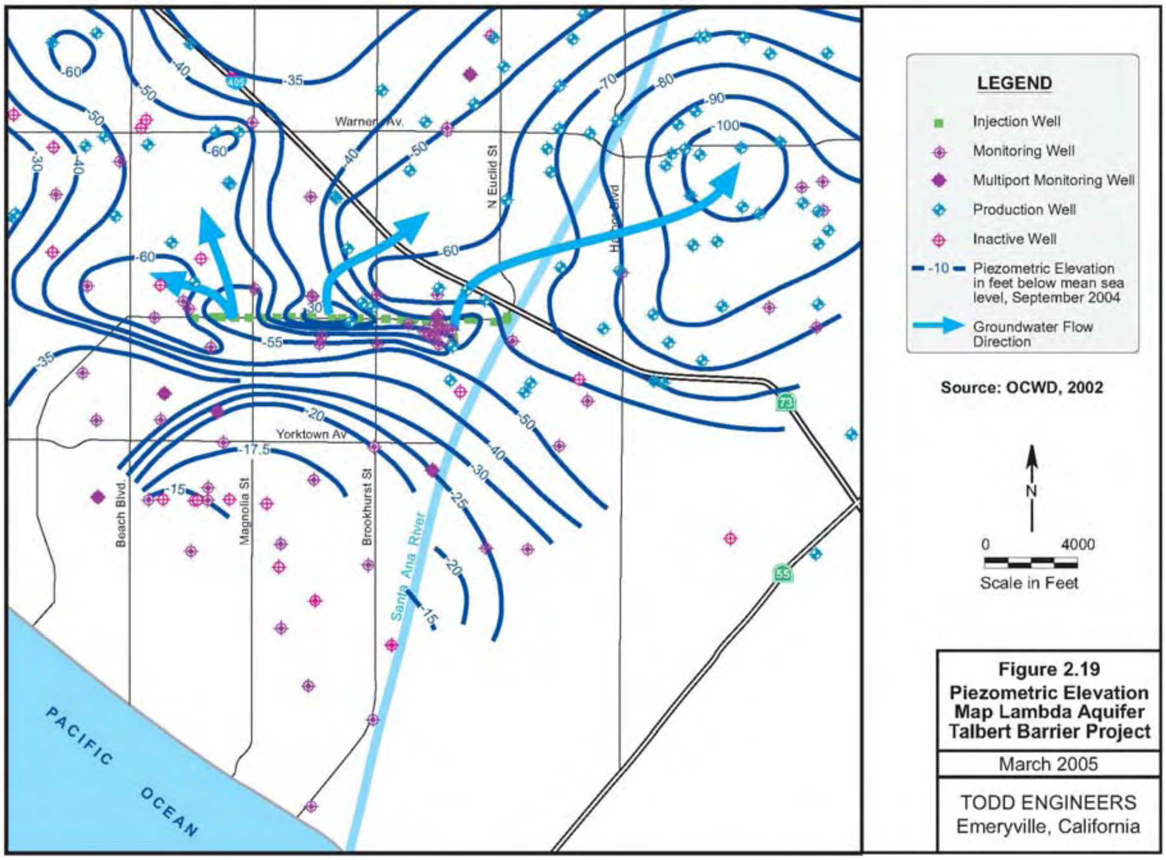


Figure 2.19. Piezometric Elevation Map, Lambda Aquifer, Talbert Barrier Project.

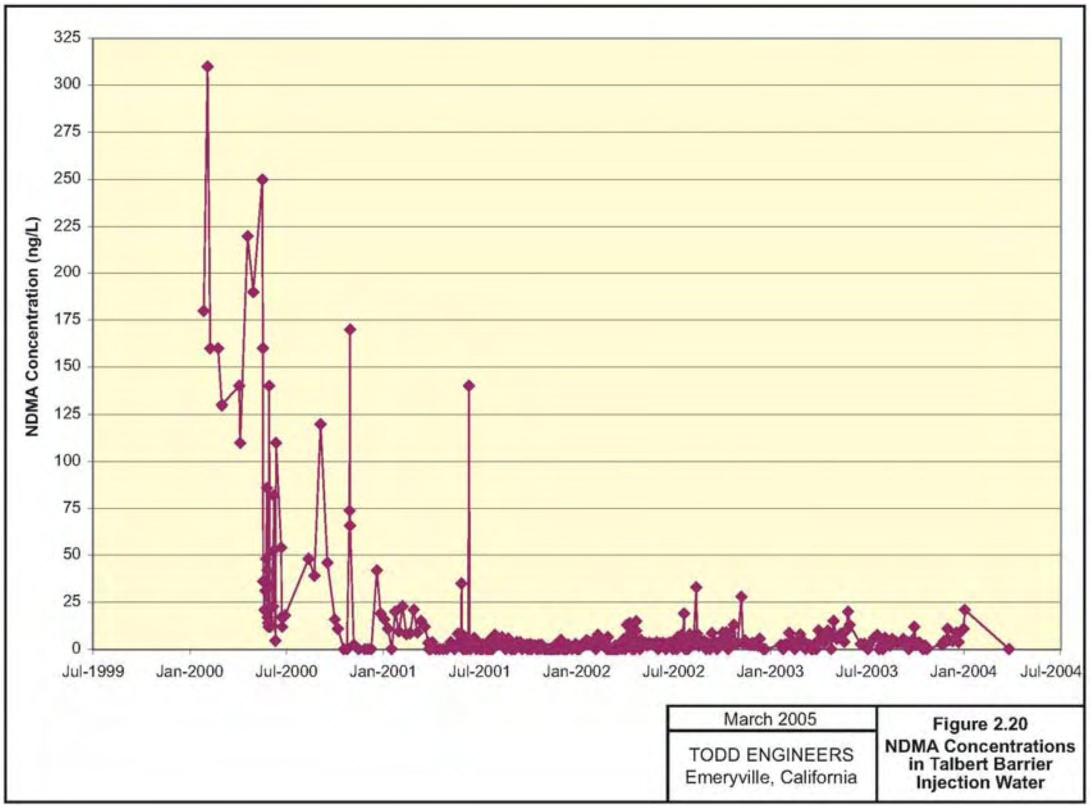


Figure 2.20. NDMA Concentrations in Talbert Barrier Injection Water.

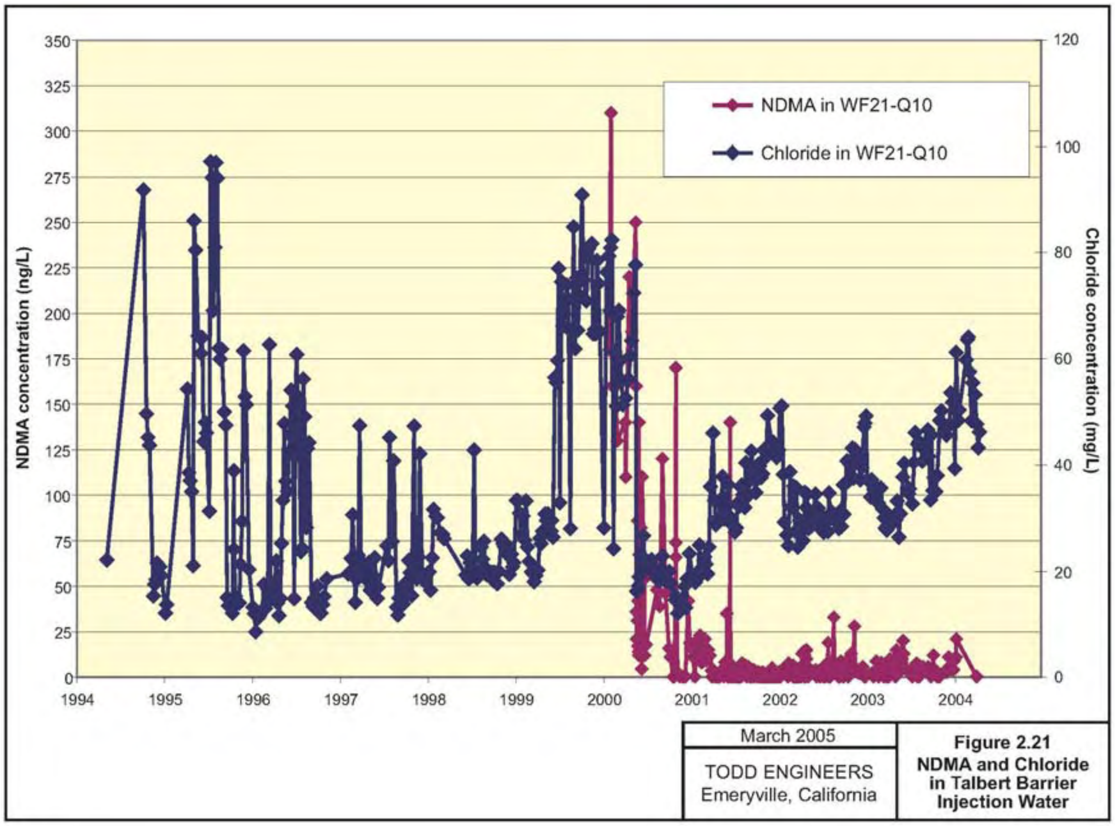
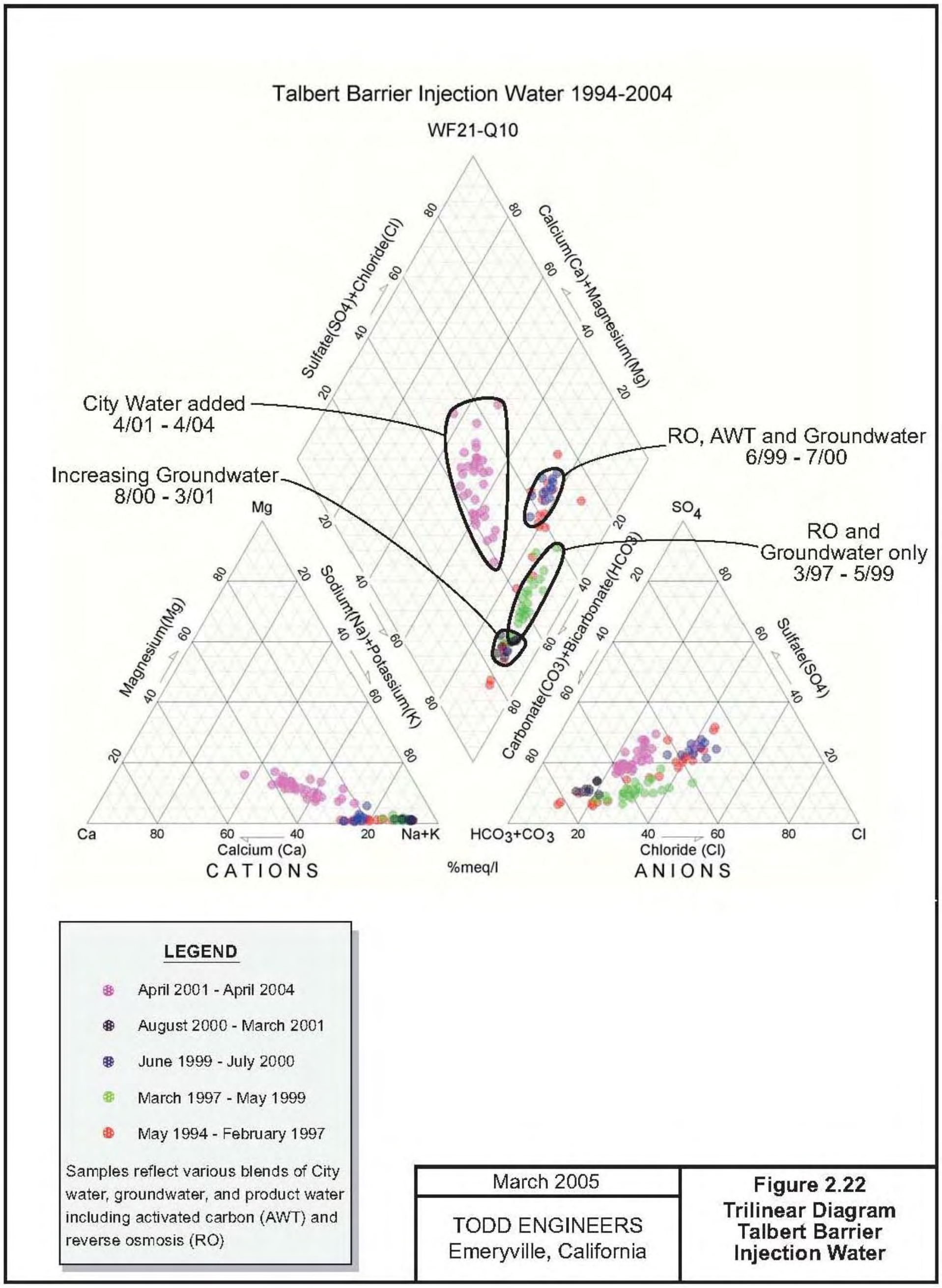


**Figure 2.21. NDMA and Chloride in Talbert Barrier Injection Water.**



Samples reflect various blends of City water, groundwater, and product water including activated carbon (AWT) and reverse osmosis (RO)

**Figure 2.22. Trilinear Diagram, Talbert Barrier Injection Water.**

Recent samples (pink dots in Figure 2.22) plot near the central portion of the trilinear and reflect an increasing amount of water from nearby city systems that was added to blend water beginning in 2001. Blend water chemistry data are also similar from August 2000 to March 2001, as shown by the relatively small grouping of the dark blue dots in Figure 2.22. This group reflects a decrease in chloride, which is also evident in Figure 2.21, and results from increasing amounts of groundwater and decreasing amounts of AWT water. The green dots reflect water chemistry from March 1997 through May 1999, when water from the AWT was completely absent from blend water (Figure 2.22). This time period also corresponds to lower chloride concentrations shown in Figure 2.21. These data indicate that AWT water is associated with higher chloride concentrations and may also correspond to higher NDMA concentrations. If this correlation can be assumed over time, it indicates that most of the NDMA injected into groundwater occurred prior to mid-1996 (when chloride concentrations were variable but relatively high) and from mid-1999 to mid-2000.

Because blend water chemistry data extend over many fields on a trilinear diagram due to changing chemistry over time, trilinear diagrams appear to be of limited use in matching groundwater samples with blend samples. Blend water is simply too variable over time to identify a trilinear diagram signature for blend water. The analysis is also complicated by the use of groundwater in the blend water.

### 2.7.6 NDMA in Groundwater

NDMA has been analyzed in groundwater samples from more than 50 locations in 111 wells (dual completions counted as two wells) in the vicinity of the Talbert Barrier. NDMA has been detected in at least one groundwater sample in 56 of the 111 wells at 28 locations. Figure 2.23 shows the locations for all wells sampled for NDMA within a 2-mi radius of the barrier; wells where NDMA has been detected in at least one groundwater sample are designated with a purple dot. Wells that have been sampled but have not contained detectable concentrations of NDMA are designated by a yellow dot.

As shown in Figure 2.23, NDMA has been detected at many of the wells near the barrier. Wells near the barrier consistently detect the highest concentrations of NDMA in the area. Although concentrations decrease significantly downgradient, NDMA detections persist. Several wells located more than 1.5 mi downgradient have contained NDMA at concentrations above the detection level of 2 ng/L. The spatial distribution of NDMA concentrations was contoured to produce a plume map, shown in Figure 2.24. The NDMA plume map represents detections in groundwater wells during 2000; if year-2000 data were unavailable, the most recent concentration was contoured.

The map in Figure 2.24 represents the maximum areal extent of NDMA detections in groundwater and the general distribution of concentrations. These contours are a composite map for all aquifer layers and do not imply that all aquifers are impacted. This is illustrated by the location of yellow dots within the overall distribution of the plume. Wells that are close to the barrier but have not detected NDMA (light dots) typically are wells with long and deep screens that are generally deeper than screens in the injection wells.

The distribution of the plume is consistent with groundwater flow patterns illustrated in Figure 2.19. The piezometric surface indicates more flow inland, resulting in a larger plume north of the barrier than south. NDMA has migrated slightly farther from the barrier to the north and east, likely due to groundwater pumping as evidenced by the depressions shown in the piezometric surface contours in Figure 2.19.

Only two groundwater wells have detected NDMA concentrations above 100 ng/L. Those two wells, M17B/1 and M21/3, are monitoring wells located adjacent to injection wells and have detected NDMA at concentrations of 180 and 140 ng/L, respectively. Five additional monitoring wells within several hundred feet of the barrier have detected NDMA in groundwater at concentrations above 50 ng/L. Although data are limited, recall that blend water in early 2000 had an average NDMA concentration of 117 ng/L. Using groundwater and blend water data and the correlation to chloride previously discussed, it seems reasonable to assume that blend water has contained approximately 100 to 200 ng of NDMA/L historically.

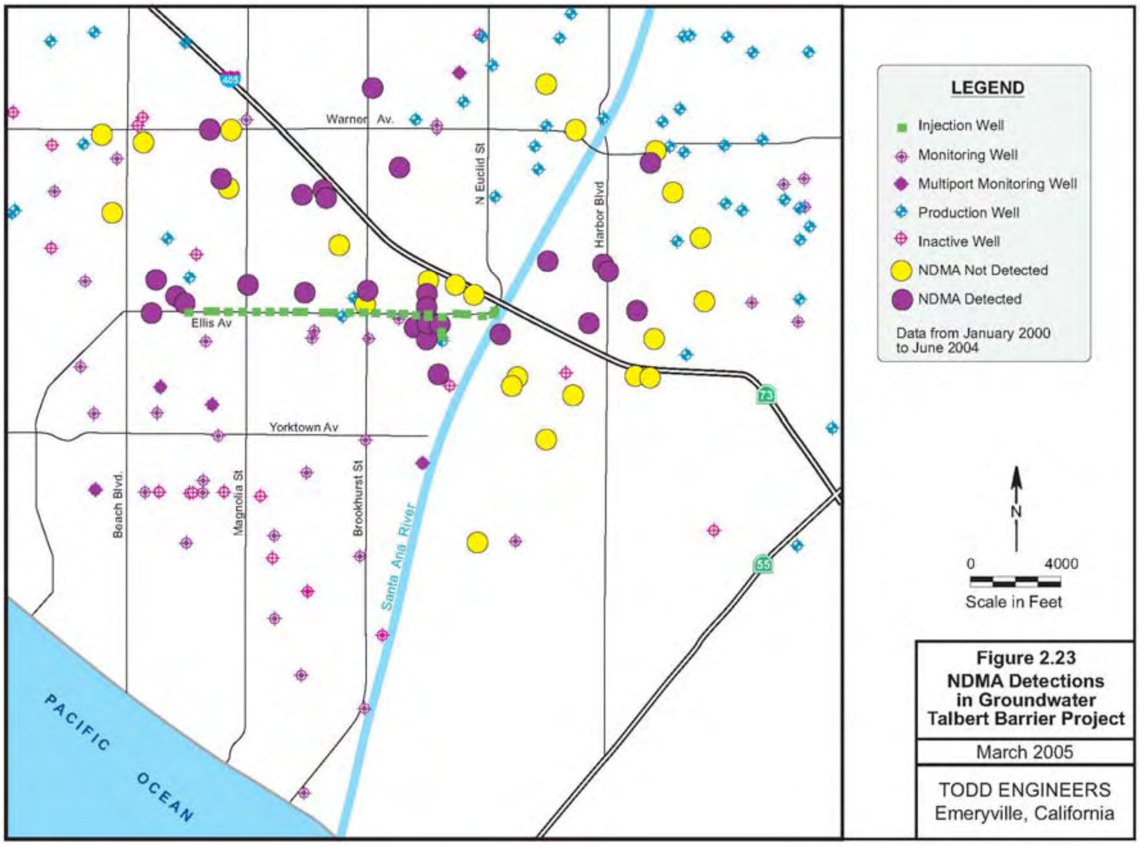


Figure 2.23. NDMA Detections in Groundwater, Talbert Barrier Project.

To examine the vertical extent of NDMA in groundwater, three cross sections were constructed. Cross section locations are shown in Figure 2.24, and cross sections are displayed in Figure 2.25. NDMA concentrations are posted beside each well screen on the cross section, but detailed concentration contours are not presented. Rather, the overall potential area of NDMA impact to groundwater is illustrated by shaded areas above a concentration of 2 ng/L. All cross sections begin at an injection well on the left side of the section and show wells downgradient from the injection well.

Cross section A-A' illustrates a decrease in NDMA concentrations from more than 100 ng/L at the barrier (assumed) to an average of 33 ng/L in OCWD M-36 several hundred feet downgradient. This decrease could be the result of dispersion, degradation, or lower-than-assumed NDMA concentrations being injected. After the initial decrease, concentrations remain relatively consistent for more than 1,200 ft downgradient to HB-Dyke 1 (NDMA concentration of 35 ng/L). These data indicate advective transport of NDMA with insignificant dispersion or degradation. The cross section also indicates that NDMA has not dispersed into the fine-grained units between the injection zones, as evidenced by the middle port of OCWD M-37, where NDMA has not been detected (Figure 2.25).

Cross section B-B' illustrates the vertical mixing of the blend water in the aquifer as pumping wells create vertical gradients. Pumping wells and other factors allow NDMA to impact groundwater below the zone of injection as blend water spreads out in the aquifer. NB-TAM S1 is a shallow well located adjacent to a deep well that has detected NDMA. These data suggest that NDMA may be transported faster in some aquifers than in others (Figure 2.25).

Cross section C-C' also illustrates the vertical spreading of blend water as evidenced by NDMA detections in wells deeper than the injection zones. Some of the vertical transport is likely related to the geologic dip of the aquifer strata into the deeper portions of the groundwater basin. This section also shows a deep well (OCWD D5) within 2000 ft of the barrier that has not detected NDMA, likely due to the deep well screen. This well illustrates how wells can be located within the NDMA contours in Figure 2.24 yet have not detected NDMA in groundwater samples (Figure 2.25).

### 2.7.7 NDMA Fate and Transport Summary

*NDMA Detections*

- NDMA concentrations in blend water have ranged from 310 ng/L to less than 2 ng/L and average 17 ng/L (standard deviation = 39) from January 2000 through April 2004. From January 2000 to June 2000, NDMA concentrations averaged 117 ng/L. After UV treatment was added in March 2001, NDMA concentrations decreased significantly to 5 ng/L.
- Historical NDMA concentrations in blend water are unknown. However, groundwater detections indicate that historical NDMA concentrations were at least as high as 180 ng/L.
- Injection water chemistry has varied significantly over time and appears to be related to the various amounts of AWT water, RO water, groundwater, and city water that have been blended for injection. Trilinear diagrams illustrate the changing signature of injection water over time.
- NDMA has been analyzed in groundwater samples from 111 wells (dual completions counted as two wells) in the vicinity of the Talbert Barrier. NDMA has been detected in at least one groundwater sample in 56 wells.

- The spatial distribution of NDMA concentrations was contoured for an NDMA plume map. The plume map is consistent with groundwater flow patterns.

*NDMA Fate and Transport in Talbert Barrier Groundwater*

- NDMA persists in groundwater and has migrated to approximately 10,200 ft from barrier wells over 28 years. These data on NDMA transport are consistent with isotopic tracer studies and suggest that NDMA is not retarded with respect to reasonable estimates of groundwater flow velocities.
- Plume maps and cross sections indicate significant vertical mixing of NDMA in the aquifer.
- In at least one portion of the aquifer, NDMA concentrations are unchanged for more than 1200 ft downgradient. This observation indicates that mass removal processes such as chemical transformation or biodegradation are not occurring in that area.
- Given the uncertainties of mass injected into the barrier and the need for a more detailed geologic investigation to calculate NDMA mass in the aquifer, a mass balance of NDMA was not conducted.

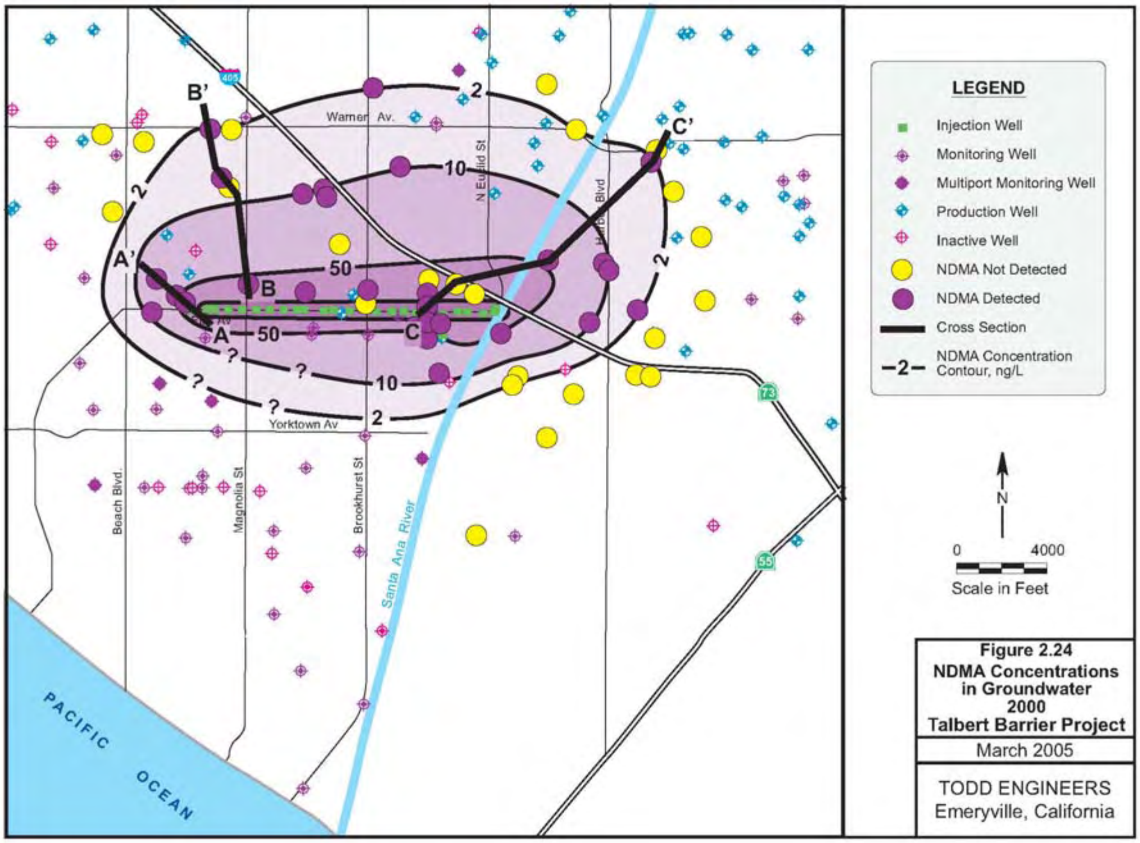


**Figure 2.24. NDMA Concentrations in Groundwater, 2000, Talbert Barrier Project.**

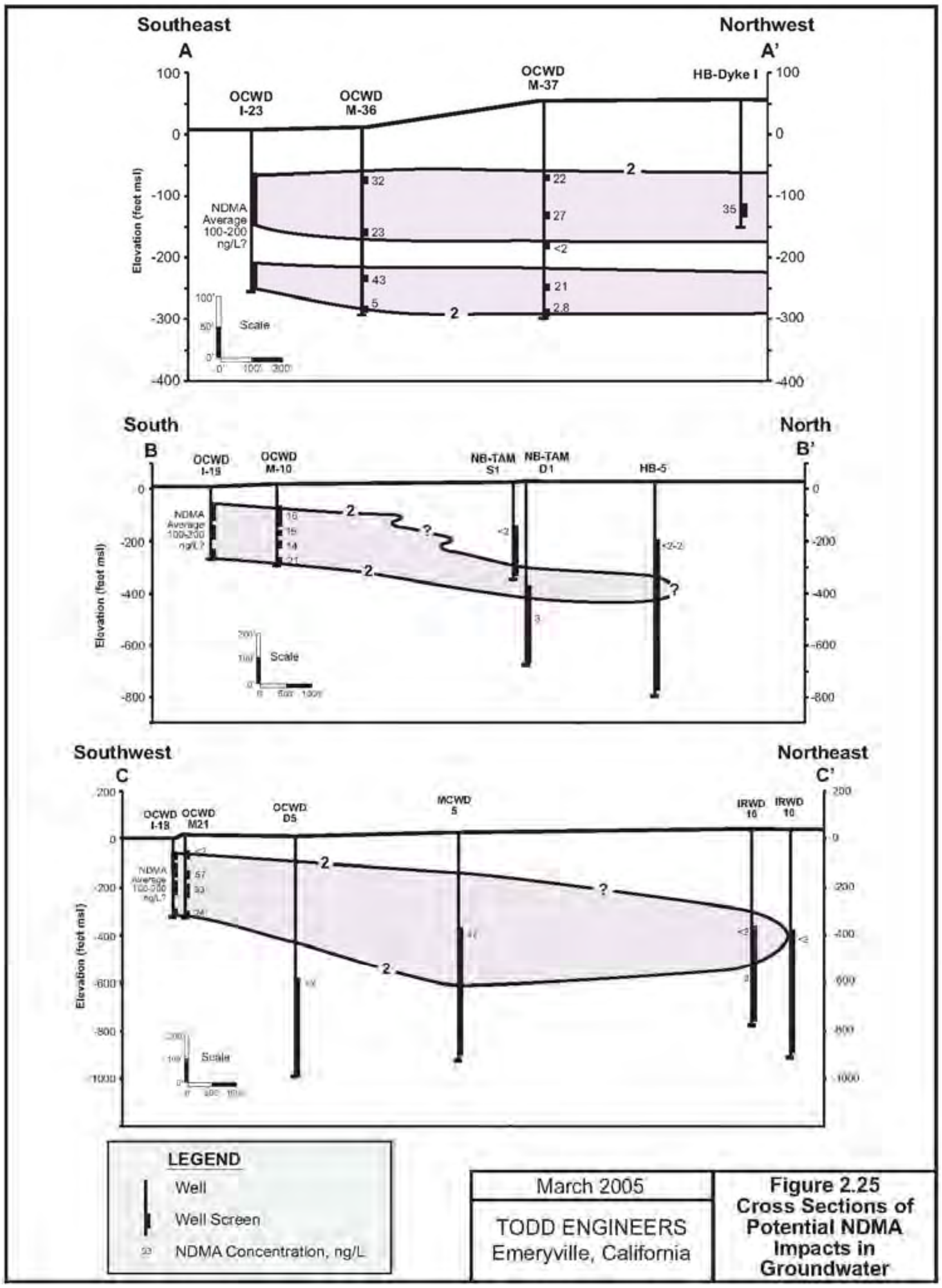


**Figure 2.25. Cross Sections of Potential NDMA Impacts in Groundwater, Talbert Barrier Project.**

## 2.8 WEST COAST BASIN BARRIER PROJECT

### 2.8.1 Introduction

West Basin Municipal Water District (WBMWD) provides wholesale potable water to more than 800,000 customers in southern Los Angeles County. It also operates the West Basin Water Recycling Program (WBWRP), which provides highly treated wastewater effluent for irrigation and specialty uses. A portion of the recycled water is used for groundwater recharge via injection wells for the prevention of seawater intrusion into the West Coast Groundwater Basin (Figure 2.2). NDMA has been detected in recycled water and several groundwater wells near the injection wells. Although an ongoing plant expansion will provide treatment to remove NDMA in the future, WBMWD has furnished data for this project to support the analysis of NDMA fate and transport in groundwater.

### 2.8.2 West Basin Water Recycling Program

The WBWRP was implemented in June 1995, with the completed construction of the West Basin Water Recycling Plant, the largest of its kind in the United States. The plant treats secondary effluent from the Hyperion Plant operated by the City of Los Angeles. Treatment varies depending on the end use but generally follows one of three different treatment trains. The Title 22 treatment train utilizes coagulation, flocculation, and disinfection, providing water for irrigation uses. The other two treatment trains, Boiler Feed and Barrier, use lime clarification and/or microfiltration, and RO technologies. The Boiler Feed treatment train provides feed water for use in high-pressure and low-pressure boilers. The Barrier treatment train provides injection water for hydraulic control of seawater intrusion.

The treatment capacity of the West Basin Water Recycling Plant has been expanded over the last 10 years; the plant produced more than $8.8 \times 10^9$ gal of recycled water during 2002–2003. An additional expansion is currently under way that will add another 5 mgd of barrier water and another 10 mgd of Title 22 water.

### 2.8.3 West Coast Basin Barrier Project

The West Coast Basin Barrier Project (Barrier Project) was constructed in the 1950s and 1960s along 8 mi of Santa Monica Bay coastline to halt seawater intrusion into basin aquifers (Figures 2.2 and 2.26). The Barrier Project is operated by the Los Angeles County Department of Public Works (LACDPW), and injection water is provided by WBMWD. Prior to the completion of the Water Recycling Plant in 1995, the injection water was 100% imported water from the MWD. Approximately 19,000 AF of water was injected into the barrier in 1991–1992.

In 1967, 77 injection wells were in operation. By 1993, the number of injection wells had almost doubled to 150 wells, located about 200 to 1000 ft apart. The injection wells are aligned generally parallel to the coast and are located approximately 2000 to 10,000 ft inland. The injection wells extend from Los Angeles International Airport in the north to the Palos Verdes Hills in the south (Figures 2.2 and 2.26) (WBMWD, 1993). No production wells are allowed within 2000 ft of the injection wells. The closest production well is 1.5 mi inland from the barrier (McGovern and Dryden, 2002).

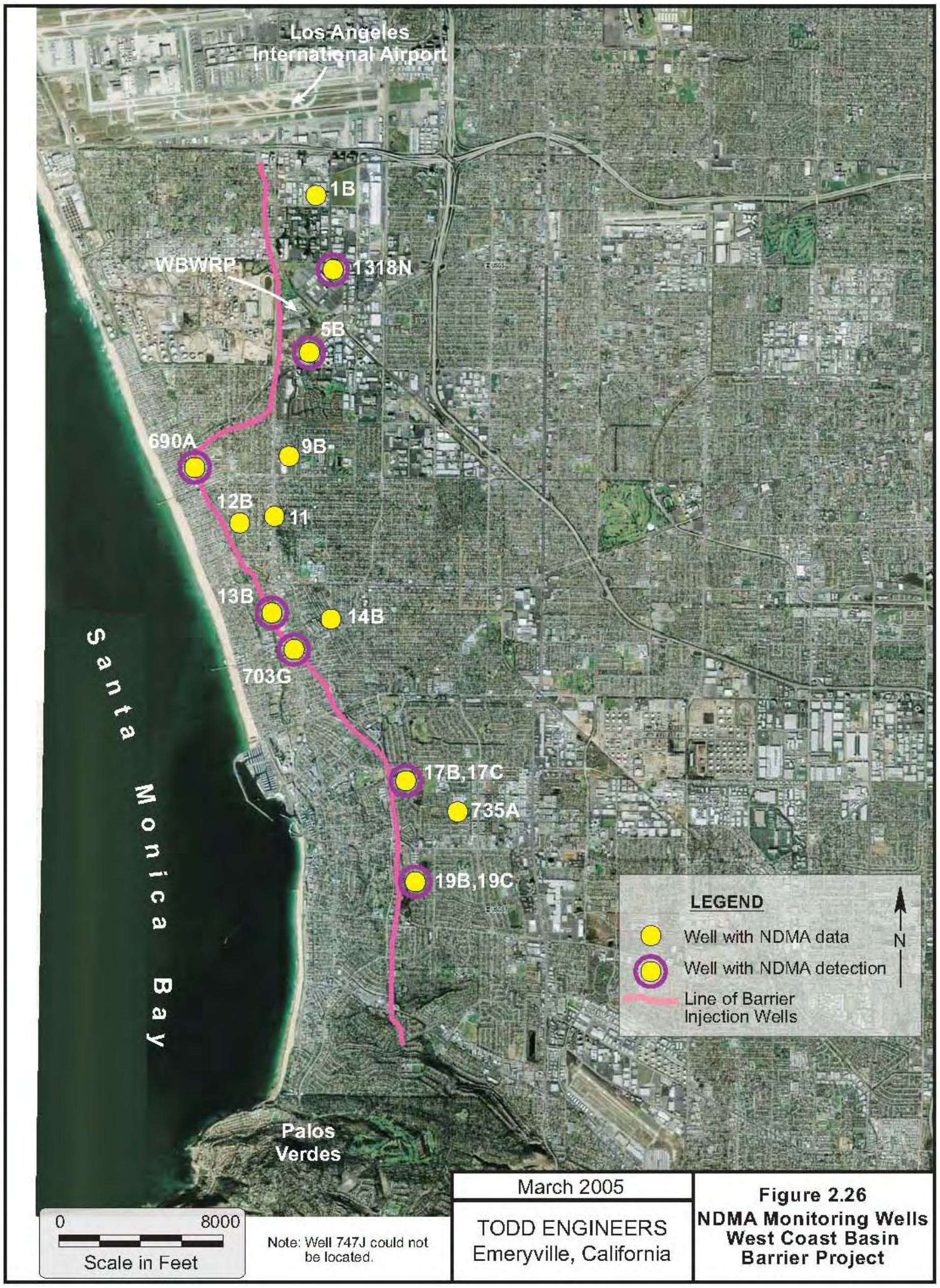


Figure 2.26. NDMA Monitoring Wells, West Coast Basin Barrier Project.

The Barrier Project consists of two sections of pressurized pipe that connect about 150 single and dual injection wells, each screened in one or more of three major aquifer packages (200-Foot Sand, Silverado, and Lower San Pedro). Water is injected into the wells through 3-in.-diameter PVC conductor pipes sized to prevent vacuums and release of dissolved oxygen. Flow rates into each well are adjusted weekly to monthly by LACDPW based on water levels and other monitoring data that indicate the effectiveness of the barrier at mitigating seawater intrusion (personal communication, LACDPW, March 2005). Because of these operational adjustments, various amounts of blend water are injected into each aquifer and/or a particular section of the barrier at any given time.

Recycled water from the West Basin Plant Barrier treatment train is blended and injected into the injection wells. Injection water is a blend of approximately 50% of recycled water from the West Basin Plant Barrier treatment train and 50% of water imported from the MWD. This injection water is referred to as “blend water” in this report. The component of blend water from the Barrier treatment train is referred to as “recycled water”; the component of blend water from MWD water is referred to as “imported water.” Recycled water and imported water are blended prior to injection.

Since 1995, WBWRP has provided about 5000 to 7500 AFY (4.5 to 6.7 mgd) of recycled water to be blended with an equal amount of imported water (McGovern and Dryden, 2002). Additional expansions of the plant are planned that will ultimately increase Barrier treatment train capacity to 17,500 AFY, an amount judged sufficient for 100% of the barrier requirement. Currently, the CDHS has provided permission to increase the use of recycled water into the barrier up to only 75% of capacity. This expansion would ultimately allow for the imported water that is currently providing 50% of the blend water to be available for other uses (McGovern and Dryden, 2002). This plant expansion would also provide for UV disinfection that would remove NDMA, which is currently detected in the Barrier treatment train water.

### 2.8.4 Hydrogeologic Setting

*Groundwater Basin and Aquifers*

The Barrier Project is located in the West Coast Groundwater Basin, a portion of the larger Los Angeles Coastal Plain (Figure 2.2). The groundwater basin covers approximately 120 sq. mi and extends along the Pacific Ocean from Santa Monica Bay past San Pedro Bay. The eastern basin boundary is the uplifted bedrock along the Newport–Inglewood fault zone, which impedes groundwater inflow from the Central Basin. The West Coast Basin connects with the Santa Monica Groundwater Basin on the north along a historically documented groundwater divide created by pumping centers. The basin extends to the Orange County line on the south.

Aquifers of sand and gravel have been delineated by previous investigators (*Planned Utilization*, 1961). Early nomenclature is still in use but has been modified somewhat with the investigation and construction of the Barrier Project. The three main aquifers used for water supply and injection along the barrier are the 200-Foot Sand, the Silverado, and the Lower San Pedro. Injection wells are screened in these aquifers at depths from about 150 to 700 ft bgs. Well construction information indicates that most of the aquifer is screened; however, many wells leave 20% or more of the aquifer unscreened, allowing blend water to mix vertically with groundwater over a zone thicker than the zone of injection.

Most of the injection wells are completed in only one aquifer, but about 10% are completed in both the 200-Foot Sand and Silverado aquifers, primarily in areas where these two aquifers are merged in the subsurface and respond as one aquifer system. Two-thirds of the barrier wells are at least partially screened in the Silverado aquifer, since most of the water supply pumping occurs in that zone. The injection well distribution in the main aquifers is as follows:

- 200-Foot Sand, 20 wells, 13%
- Silverado, 85 wells, 57%
- 200-Foot Sand and Silverado aquifers, 15 wells, 10%
- Lower San Pedro, 30 wells, 20%

Aquifer thicknesses vary significantly along the barrier and inland. Cross sections prepared by LACDPW and the DWR (*Planned Utilization*, 1961) indicate that the Silverado Aquifer thickens to the south and east.

### *Groundwater Flow*

Groundwater occurs in the Coastal Plain under unconfined and confined conditions. Historical flow directions were westward as groundwater discharged into the ocean prior to the significant pumping of groundwater in the area. With increased pumping, inland water levels fell below sea level and allowed seawater to intrude into the aquifers. With the installation and operation of the Barrier Project in the 1960s, hydraulic gradients have been reversed locally and a groundwater mound along the barrier line generally prevents inland movement of seawater (although leaks have been documented in some areas). Injection water also flows eastward, replenishing aquifers that have been overpumped.

Recent groundwater flow patterns are indicated by the water level contours for spring 2001 in Figure 2.27, prepared by the WRD for the Los Angeles Coastal Plain. Water levels in the West Coast Basin vary from about 10 ft above sea level near the barrier to 90 ft below sea level east of the barrier along the Newport-Inglewood uplift (eastern boundary of the West Coast Basin). As shown by the arrows (added to the WRD map for emphasis), groundwater flows eastward in the West Coast Basin away from the barrier wells. Injection water accounts for more than one-half of the total inflow into the West Coast Basin (average inflow for the period 1970–1996) (WBMWD, 2002).

An isotopic study conducted by WBMWD in 1999 indicated groundwater velocities of 100 to 500 ft per year (0.3 to 1.4 ft/day). No information was available on which aquifers were sampled for the study, but well locations indicate that several Silverado wells were included. Using transmissivity and hydraulic conductivity data from published information for the Silverado aquifer (*Planned Utilization*, 1961), a higher velocity (about 2 ft/day) east of the barrier is indicated. Applying the shortest travel time indicated in the 1999 study of 1.4 ft/day, blended water may have migrated more than 4000 ft away from the barrier in some areas by 2004 (8.5 years since the injection of blend water began in mid-1995).

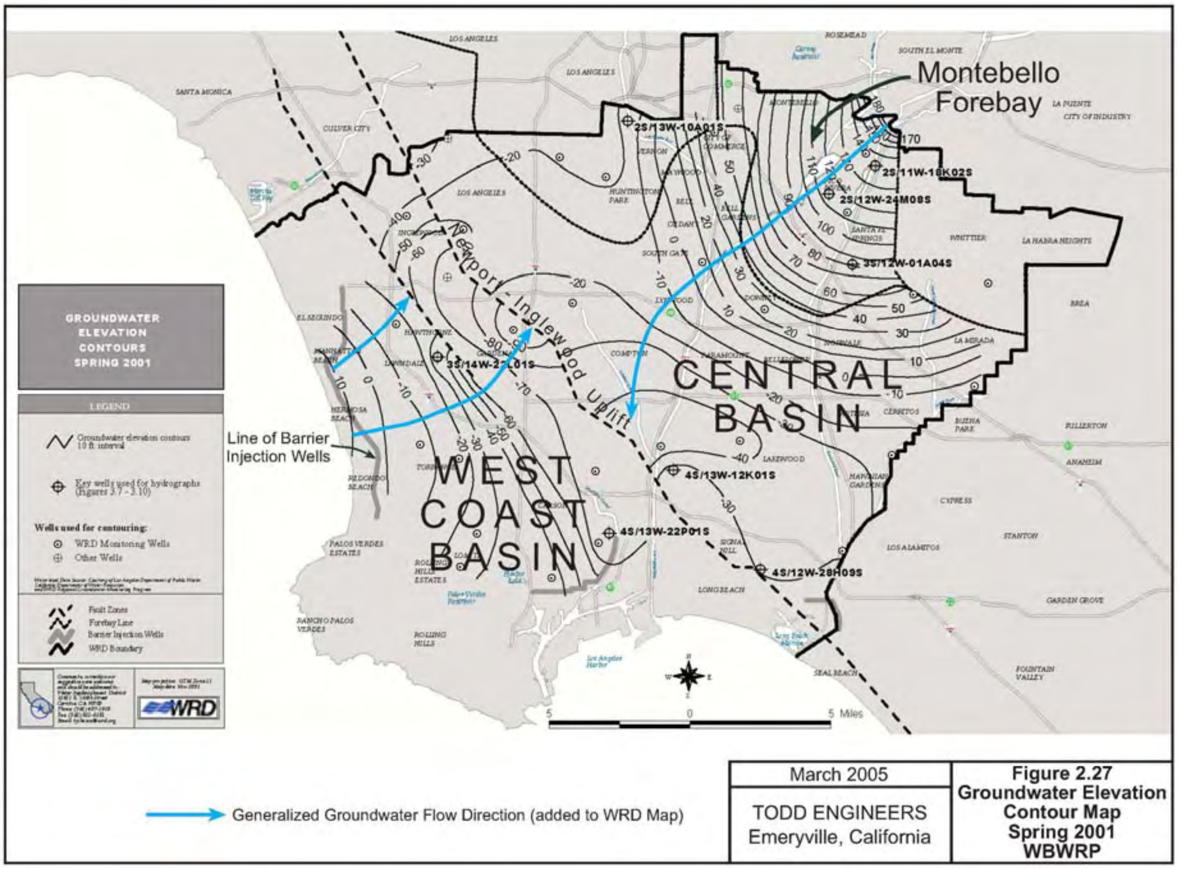


**Figure 2.27. Groundwater Elevation Contour Map, Spring 2001, WBWRP.**

### 2.8.5 Available Data

Water quality data, engineering reports, and information on the operation of the water recycling program were supplied by WBMWD. Well construction data and information on the operation of the Barrier Project were also compiled and provided by the WBMWD and supplemented with data from LACDPW. Electronic files for well locations in Geographical Information System (GIS) format were available from CH2M Hill, which had compiled these files for a groundwater monitoring plan. Available data were supplemented with general references on hydrogeology compiled by Todd Engineers. Specific data sets are described in more detail below. A list of references used for the project is provided at the end of the report.

*NDMA Data*

NDMA data were provided for the West Basin Water Recycling Plant influent samples, Barrier treatment train product water, blended water, and other sampling stations within the treatment process from July 2000 through March 2003. Samples were collected on a weekly to monthly basis and analyzed at sufficiently low detection levels (2 ng/L) to characterize NDMA concentrations in both Barrier treatment train water as well as blended water. NDMA data for imported water were available on a monthly basis from April 2002 through February 2003.

NDMA testing has been conducted in 30 groundwater monitoring wells from as early as July 1995, the beginning of the recycling program. However, prior to about 1999, laboratory method detection levels were too high (1000 ng/L) to detect the range of NDMA concentrations that exist in blend water and groundwater. Detection levels were lowered in 1999, first to 30 ng/L and then to 1 ng/L, providing usable NDMA data for 16 wells. Data are available from May 1999 through September 2003, but sampling frequency and data vary from well to well.

*Additional Water Quality Data*
Inorganic and organic water quality data were provided for 30 groundwater wells from 1995 to 2004 with various sampling frequencies, although quarterly data are available for most of the wells. Groundwater analyses were conducted for trace metals (EPA Method 200.8); major anions; cations, including nitrogen species; and physical parameters, including pH and temperature. Data for organic constituents were also included, but not all constituents were analyzed on a quarterly basis (EPA Methods 524.2, 525.1, and 625). Additional water quality data were also available for treatment plant water sampled at various stages of treatment on a weekly to monthly basis. Data for major anions and cations were available for blend water for 1995 and 1996. Data also included pH, free and total chlorine, nitrogen (as nitrate, nitrite, and ammonia), and total organic carbon (TOC) measurements in plant and blend water.

*Data Use*
Water quality data provided by WBMWD were generally available in electronic formats, typically consisting of separate Excel spreadsheets for each year or quarter, and for each media sampled. These data were provided in various formats in 39 Excel workbooks. Separate worksheets and workbooks were combined and consistently formatted into an Access database to facilitate the analysis. Electronic data were supplemented with additional water quality data extracted from paper copies of time–concentration plots in a WBMWD engineering report (McGovern and Dryden, 2002). Where data were sufficient, geochemical plots were constructed to differentiate between different water types/sources and to analyze water quality changes over time.

### 2.8.6 NDMA in Source Water

Samples of recycled water (Barrier treatment train effluent) and blend water have consistently contained detectable concentrations of NDMA since lower detection levels (usually 1 ng/L) were established in 2000. From July 2000 through February 2003, NDMA concentrations in the blend water ranged from 6 to 1190 ng/L, with an average concentration of 62 ng/L (standard deviation of 115). NDMA data for blend water and imported water are presented in Figure 2.28. The maximum concentration of 1190 ng/L does not appear to be representative of the higher concentrations; the second highest concentration is 380 ng/L. NDMA concentrations in recycled water are not presented but are higher than in blend water by about a factor of 2, given that 50% of blend water consists of recycled water.

As shown in Figure 2.28, concentrations of NDMA are highly variable over time and can generally be characterized by two time periods when concentrations were statistically different. From July 2000 through about March 2001, NDMA concentrations were generally higher and more variable, averaging 148 ng/L with a standard deviation of 237. Since March 2001, concentrations have been lower and less variable, with an average of 41 ng/L and a standard deviation of 32. In general, concentrations were lowest between January 2002 and August 2002, with an average concentration of 22 ng/L during that time period.

NDMA has also been detected in imported water that is used to blend with recycled water before injection (Figure 2.28). Available data from March 2002 to February 2003 showed that concentrations ranged from 2.2 to 10 ng/L and averaged 4.7 ng/L. Although imported water contains lower NDMA concentrations than does recycled water, imported water does represent a detectable component of NDMA being injected in the barrier. Data are limited, and NDMA concentrations in pre-2002 imported water are unknown. If NDMA occurred in imported water before 1995, then NDMA was introduced into the aquifer system prior to the injection of blend water.

### 2.8.7 NDMA in Groundwater

Since 1999, NDMA has been analyzed in 16 groundwater monitoring wells at sufficiently low detection levels to characterize impacts to groundwater. (For purposes of discussion, Wells 17B/17C and 19B/19C are counted as four wells even though they represent dual completions at two locations). Of the 16 wells, NDMA has been detected in eight wells at concentrations ranging from 2.0 ng/L to 110 ng/L. These data are summarized in the following table; wells detecting NDMA are highlighted. Wells can be located in Figure 2.26 and are generally arranged in the table below by location from north to south.

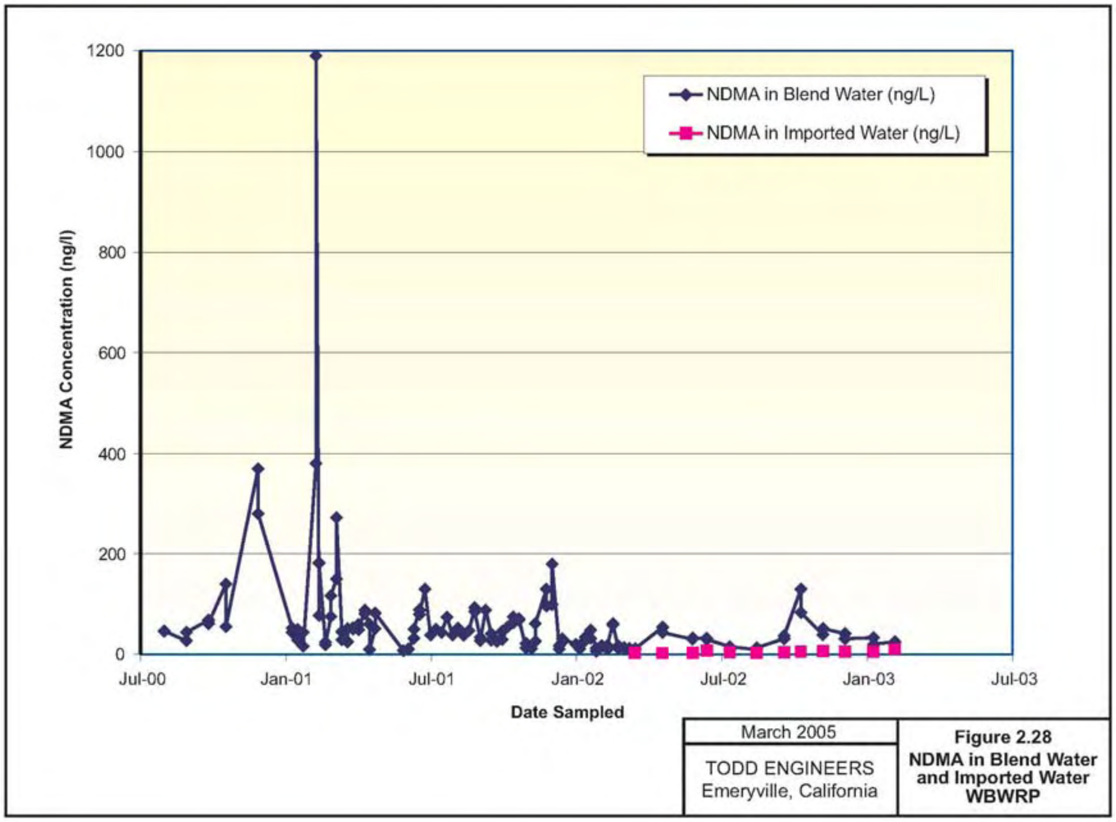


**Figure 2.28. NDMA in Blend Water and Imported Water, WBWRP.**

**Table 2.9. NDMA in Groundwater - WBWRP[1]**

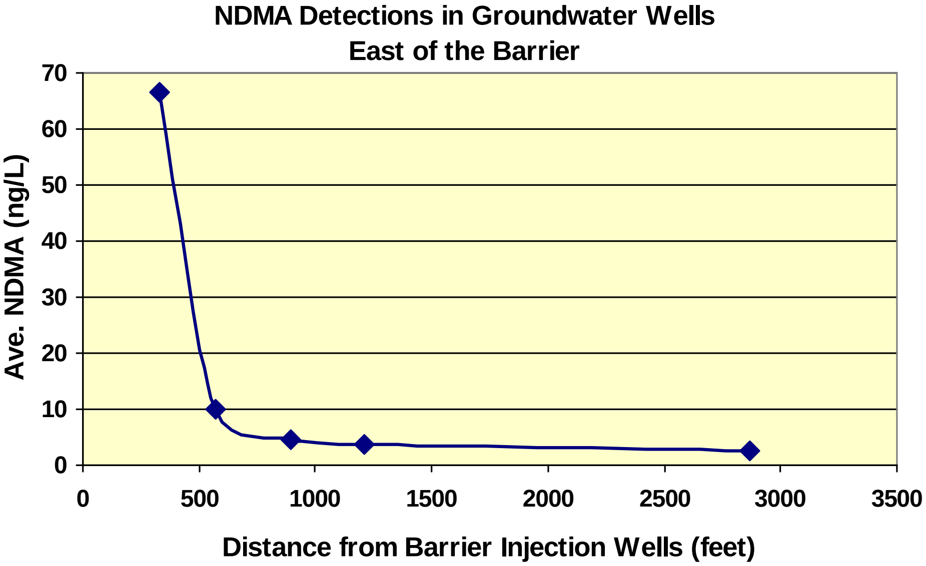
| Well | Aquifer | Distance from injection wells (ft) | No. of NDMA samples | No. of NDMA detections | Minimum NDMA concn (ng/L) | Maximum NDMA concn (ng/L) |
|---|---|---|---|---|---|---|
| 1B | Silverado | 2347 | 8 | 0 | | |
| 1318N | Silverado | 2866 | 18 | 1 | 2.6 | 2.6 |
| 5B | Silverado/ 200-Foot | 1208 | 8 | 1 | 3.8 | 3.8 |
| 9B | Silverado | 2162 | 7 | 0 | | |
| 690A | Silverado/ 200-Foot | 450* | 18 | 3 | 2.0 | 3.7 |
| 11 | Silverado | 2193 | 16 | 0 | | |
| 12B | Silverado | 641 | 16 | 0 | | |
| 13B | Silverado | 328 | 11 | 11 | 44 | 110 |
| 14B | Silverado | 1850 | 7 | 0 | | |
| 703G | Silverado | 391* | 18 | 2 | 2.1 | 5 |
| 17B | Silverado/ 200-Foot | 570 | 19 | 18 | 3.9 | 17 |
| 17C | LSP | 570 | 19 | 1 | 2.0 | 2.0 |
| 735A | LSP | 3075 | 5 | 0 | | |
| 19B | Silverado | 892 | 11 | 0 | | |
| 19C | LSP | 892 | 11 | 1 | 4.7 | 4.7 |
| 747J | Unknown | 7000 | 1 | 0 | | |

[1]Well is west of the barrier;
LSP, Lower San Pedro.

As shown in the table, NDMA has been detected in each of the three aquifer systems but generally at much lower concentrations than in blend water (with the exception of higher concentrations in Well 13B). NDMA has been detected in all monitored wells that are within 600 ft of any injection wells. NDMA concentrations are highest in the well closest to the injection wells (Well 13B) but decrease dramatically in other wells with distance from the barrier. NDMA is not detected in several wells that would be expected to exhibit impacts, given reasonable transport times. Because of limited data, low concentrations, and sporadic detections, it was determined that plume maps could not be constructed in sufficient detail to provide useful information.

Well 13B, which has NDMA concentrations ranging from 44 to 110 ng/L, is an “internodal well,” a term that refers to a location between two injection wells along the barrier. Although 328 ft from the closest injection well, Well 13B’s internodal location likely accounts for the higher concentrations, since the likelihood of being impacted by a high percentage of injection water is increased (receiving injection water from two directions). With the exception of Well 13B, NDMA concentrations in groundwater wells have been much lower than in blend water (average, 62 ng/L). The average concentration for all NDMA detections in groundwater is 12 ng/L (average decreases to 4.3 ng/L when the higher concentrations in Well 13B are excluded).

For wells more than 600 ft downgradient from the barrier, NDMA detections are sporadic and not well correlated to distance. The two wells west of the barrier have lower NDMA concentrations than expected, given their proximity to the barrier; this is likely the result of different transport conditions, since seawater intrusion has reversed gradients west of the barrier groundwater mound. If only eastern wells that have detected NDMA detections are plotted as a function of distance, a more predictable correlation with distance is observed as shown in the following plot:



The distance–concentration relationship is not exact because NDMA has not been detected in several wells close to the barrier. In addition, average NDMA concentrations do not reflect the sporadic nature of the detections, since concentrations are so close to detection limits. Nonetheless, the graph illustrates the downgradient distance at which NDMA has been detected and at what concentrations. Except for detections in two wells, NDMA concentrations have been generally close to the detection limits of the analytical methods.

### 2.8.8 NDMA Fate and Transport

Isotopic studies and groundwater modeling conducted by WBMWD indicate that injected water is transported at velocities ranging between 0.3 and 1.4 ft/day. Using the transport time of 1.4 ft/day, blend water with NDMA would be expected to be transported approximately 4300 ft from the beginning of injection through 2003, the most recent NDMA data in the database. These transport times are general, and NDMA concentrations in monitoring wells can vary greatly, depending on numerous factors affecting the fate and transport, including the following:

- variability in hydraulic conductivity and hydraulic gradients
- variability in aquifer thickness or other aquifer heterogeneity leading to variable transport times in each aquifer
- variability in amount of blend water injected into each aquifer
- variability in amount of blend water injected into each section of the barrier along the 8-mi line of injection wells
- variability of NDMA concentrations in the blend water
- variability of NDMA impacts to the aquifer from imported water prior to injection of blend water
- construction of the injection and monitoring wells
- injection well condition such as well efficiency, clogging, or other factors
- surface recharge near the well
- lateral and vertical dispersion of NDMA in the aquifers

- mixing of impacted water and unimpacted water in well samples near the leading edge of the blend water
- degradation of NDMA in the distribution system
- degradation of NDMA in the saturated zone

In order to differentiate among some of these possible fate and transport processes, groundwater quality data were evaluated for presence of blend water by using constituents other than NDMA. This was accomplished through review of previous WBMWD studies on tracers of groundwater flow and mixing models, as well as the independent construction and analysis of time–concentration plots and trilinear diagrams by using the water quality database.

A 1999 isotopic study conducted by WBMWD attempted to quantify the mixing of injection water and groundwater in monitoring and production wells downgradient of the barrier. The study applied a two end-member mixing model of oxygen isotope data ($\delta^{18}$O) based on $\delta^{18}$O values expected for local recharge (infiltration of precipitation) and injection water (imported water that had been injected into the barrier over the last 40 years, including blend water) (Davisson et al., 1999). Local recharge was further corroborated by detections of methyl tert butyl ether (MTBE), a gasoline component thought to be coming from sources at the surface.

The study suggested that most samples were composed of a mixture of injection water and groundwater. Even after decades of injection at the barrier, only one well (a monitoring well very close to the barrier) appeared to contain more than 90% injection water. The remaining samples from monitoring wells contained mixtures from 53 to 69% injection water. Water samples from nearby production wells contained even smaller percentages of injection water (0 to 43%), presumably because of the longer distance from the barrier and longer screen intervals that tap nonimpacted areas of the aquifers. Some uncertainty in a quantitative mixing model is likely due to the variability of $\delta^{18}$O in injection water over time. For example, imported water was thought to have a $\delta^{18}$O value different from the $\delta^{18}$O value of blend water. In addition, various mixtures of imported water sources (Colorado River water and State Water Project water) have been injected over time, perhaps resulting in various $\delta^{18}$O values. Nonetheless, if significant mixing is occurring as indicated, this process could explain some of the lower-than-expected NDMA concentrations observed in groundwater.

In a 2003 monitoring plan, CH2M Hill evaluated various water quality constituents to use as surrogates or “tracers” for injected blend water (CH2M Hill, 2003). It noted that chloride levels in previously injected water (imported water) were higher than in blend water. It also proposed using other constituents such as boron to supplement chloride in the mixing analysis. Chloride could not be used as a tracer for all wells because of the impacts from seawater intrusion seen in many wells. However, the use of chloride data appeared to have merit in the evaluation of one nearby well, Well 17B. When chloride and boron were used, Well 17B water was interpreted as becoming 100% blend water about 2.75 years after blend water injection began, a transport time consistent with the isotopic study and groundwater modeling.

If Well 17B can be assumed to contain a high percentage of blend water as indicated in the 2003 study, then the relatively low NDMA concentrations in Well 17B (average, 10 ng/L) are unlikely to be the result of mixing or dispersion alone. This may indicate that some degradation of NDMA has occurred between the blend water sampling point and the monitoring well. However, this conclusion is uncertain, given the high variability of NDMA in source waters and the uncertainty in a quantitative mixing model.

### 2.8.9 Geochemical Plots

To further analyze the data with respect to the fate and transport of NDMA in the aquifer, geochemical plots including time–concentration graphs and trilinear diagrams were constructed for selected constituents in groundwater. A discussion of these analyses is provided below. Selected trilinear diagrams are provided as examples.

*Blend Water and Imported Water*
Water quality differences are evident between recycled water and imported water. On average, total dissolved solids (TDS) are lower in recycled water (100 mg/L) by about a factor of 5. Chloride is also lower; historical average values for blend water are reported as 60 mg/L compared to about 90 mg/L in imported water (CH2M Hill, 2003). Nitrogen compounds, including nitrate, and TOC are also less concentrated in recycled water than in imported water.

To evaluate the overall water quality signature, concentrations of major anions and cations for blend water and imported water were converted to milliequivalents per liter (meq/l) and plotted on trilinear diagrams (Figure 2.29).

Data plotted for the blend water are from 1995 and 1996, the only data with sufficient anions and cations for a trilinear analysis. Although only early data are included in the analysis, these data contained the highest concentrations of NDMA and are likely the waters that have migrated to NDMA-impacted wells. Because full inorganic water quality data were unavailable for imported water, historical (pre-1995) well data were used as a surrogate. Historical data from a well near the barrier (703G) and interpreted to be impacted by imported water from injection were compared to constituents of imported water and found to be similar. These data also compared favorably to data from several other wells where impacts from pre-1995 injection water were evident. Even if samples contained a mixture of imported water and groundwater, they are representative of pre-blend water injection and sufficient for a qualitative analysis.

As shown in Figure 2.29, the overall water types of the two groups vary only slightly (central diamond), and some samples of blend water and imported water overlap. If the water types were significantly different, then data from groundwater wells could be plotted to see which source the wells resemble most. However, blend water and imported water are judged to be too similar with respect to water type (central diamond) to differentiate between the two sources in groundwater samples.

However, a more distinct difference is evident in the anion signature of the two waters (triangle on the lower right, Figure 2.29). For the early blend water, the contribution from sulfate as a percentage of milliequivalents per liter is higher than in imported water. The anion signatures appear to plot in sufficiently different fields to allow for comparison to groundwater samples. If the well data plot closer to blend water than to imported water, then blend water may be impacting the well. If the well data plot closer to the imported water, then the sample may contain more imported water than blend water. Plots between the two indicate mixing. Plots away from these areas may indicate native groundwater.

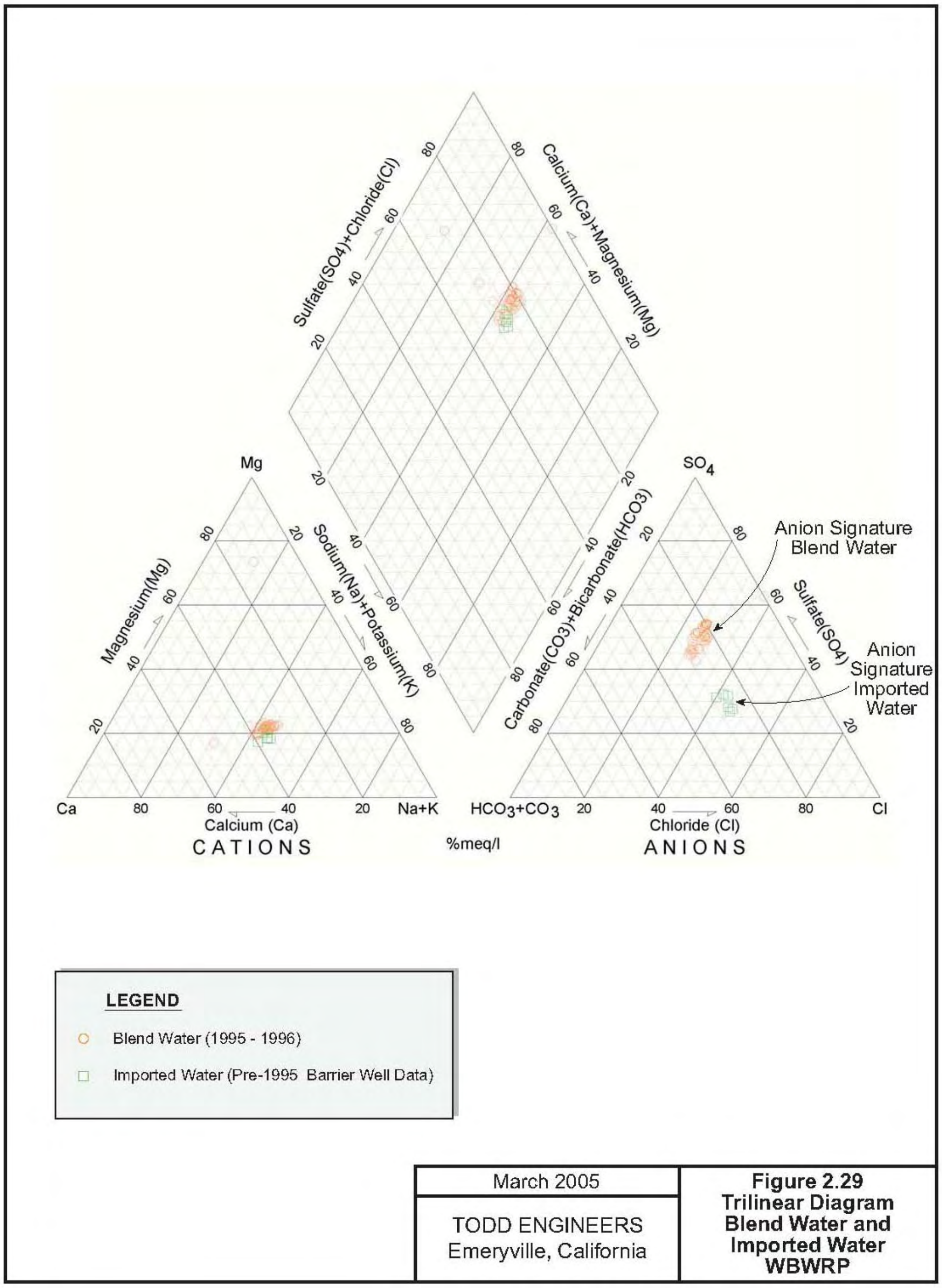


**Figure 2.29. Trilinear Diagram, Blend Water and Imported Water, WBWRP.**

The trilinear signatures of monitoring well data were compared to the signatures for blend water and imported water. Results of these comparisons, along with other observations on well water quality, are summarized for selected wells below.

*Monitoring Well 13B*

Well 13B, a Silverado well located 328 ft from the barrier, has contained the highest concentrations of NDMA of any monitoring well in the program (Table 2.9). NDMA concentrations have averaged 66 ng/L over a range from 44 to 110 ng/L, very similar to the NDMA concentrations in the recycled-water blend (average, 62 ng/L).

The well was first monitored for NDMA at sufficiently low detection levels in November 2001. The recycled-water blend had presumably already arrived at the well at that time, since the NDMA concentration was 88 ng/L. This assumption is consistent with transport times, given the well's nearness to injection wells (328 ft). Assuming an average transport time of about 1.4 ft/day, recycled water would have arrived at the well in early 1996, about eight months after recycled-water injection began in June 1995.

Figure 2.30 is a trilinear diagram showing water quality data for Well 13B, blend water, and imported water. Well 13B data are from October 1995, February 1996, and May 1996, just after completion of the WBWRP and initiation of blend water injection. These data for Well 13B (central diamond in Figure 2.30) show the inorganic water quality becoming more similar to that of blend water from October 1995 to May 1996. The cation signature shows a similar trend (lower left triangle in Figure 2.30). The anion signature suggests that Well 13B water chemistry is more similar to that of blend water than to that of imported water (lower right triangle in Figure 2.30).

Because NDMA concentrations in Well 13B are very similar to those in blend water, and because limited inorganic data are consistent with blend water increasing in the well from 1995 to 1996, it appears that the NDMA detected in Well 13B is from the blend water. Further, the elevated NDMA concentrations in Well 13B that were very similar to NDMA concentrations in blend water indicate that NDMA has not degraded significantly in the groundwater in this area. Additional inorganic water quality data for blend water and Well 13B during the time period that NDMA has been detected would be useful in further supporting these conclusions.

*Monitoring Well 17B*

With the exception of one sampling event, Well 17B has consistently contained detectable concentrations of NDMA since first sampled in May 1999. NDMA detections range from 3.9 ng/L to 17 ng/L (Table 2.9) and average 10 ng/L. Only Well 13B has higher average and maximum NDMA concentrations.

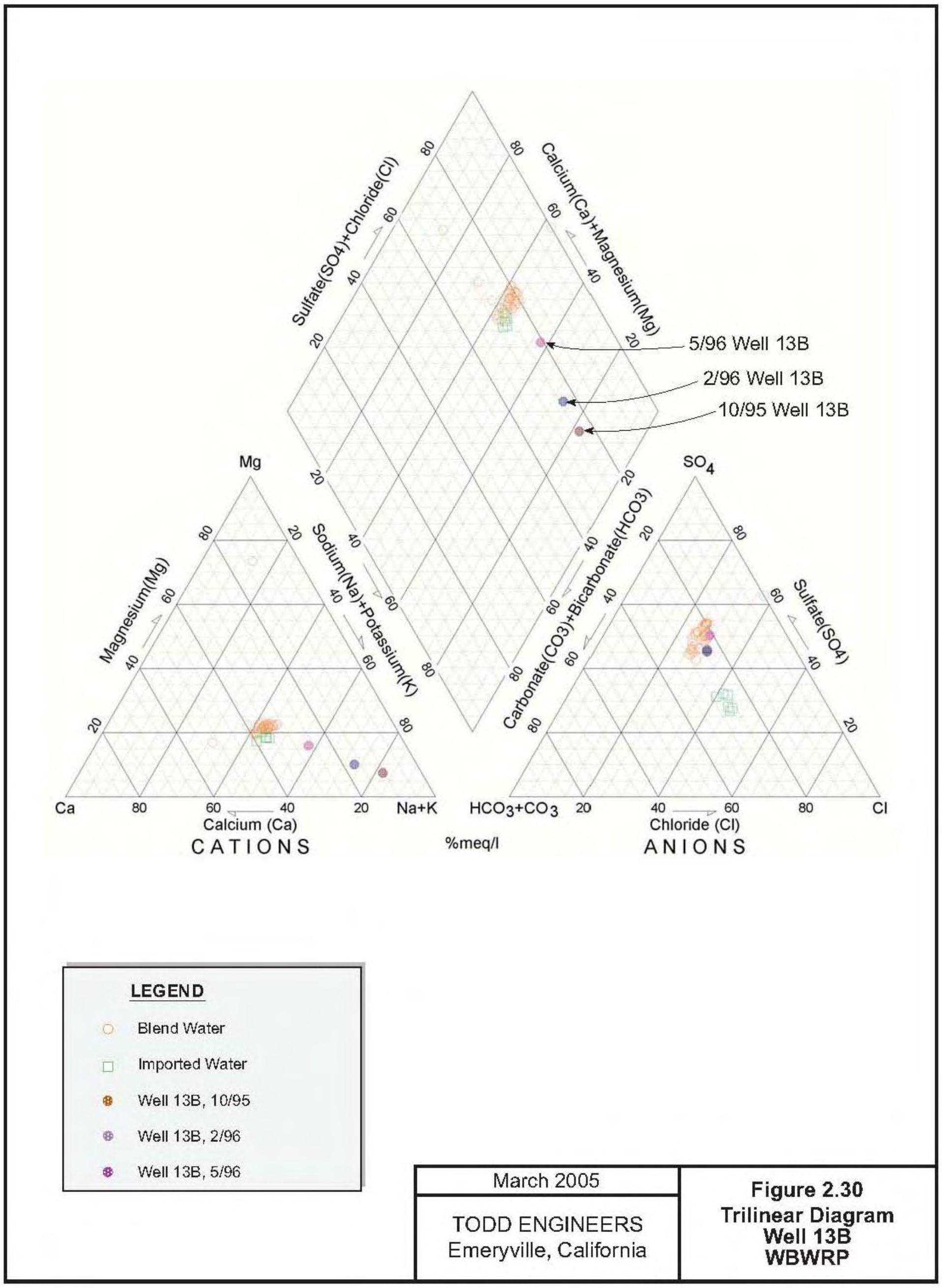


**Figure 2.30. Trilinear Diagram, Well 13B, WBWRP.**

Figure 2.31 shows time–concentration plots for chloride and boron for Well 17B. As shown on the time–concentration plot, changes to water chemistry are noted approximately 2 years after recycled water was first injected and were manifested by a gradual lowering of chloride concentrations accompanied by a gradual increase in boron concentrations. CH2M Hill (2003) correlated these changes with the breakthrough of blend water.

For further analysis, inorganic water quality data from Well 17B were plotted on trilinear diagrams with the signature of blend water and imported water (Figure 2.32). Data from Well 17B are plotted with colors varying over time to differentiate between early and more-recent sampling events. In 1995, before the influence of blend water would be expected, the anion signature (lower right triangle in Figure 2.32) plotted closer to imported water. Samples from 1998 and 1999 appear more similar to blend water and overlap the blend water data. More recent samples appear to be changing somewhat, perhaps related to changes occurring in blend water that are not plotted for lack of data.

A lack of recent data for blend water limits the analysis. However, 1999 data are consistent with the interpretation that Well 17B was significantly impacted with blend water during that time. If so, then NDMA concentrations in Well 17B should approximate NDMA concentrations in blend water. However, they are lower (10 vs 62 ng/L), suggesting some degradation of NDMA.

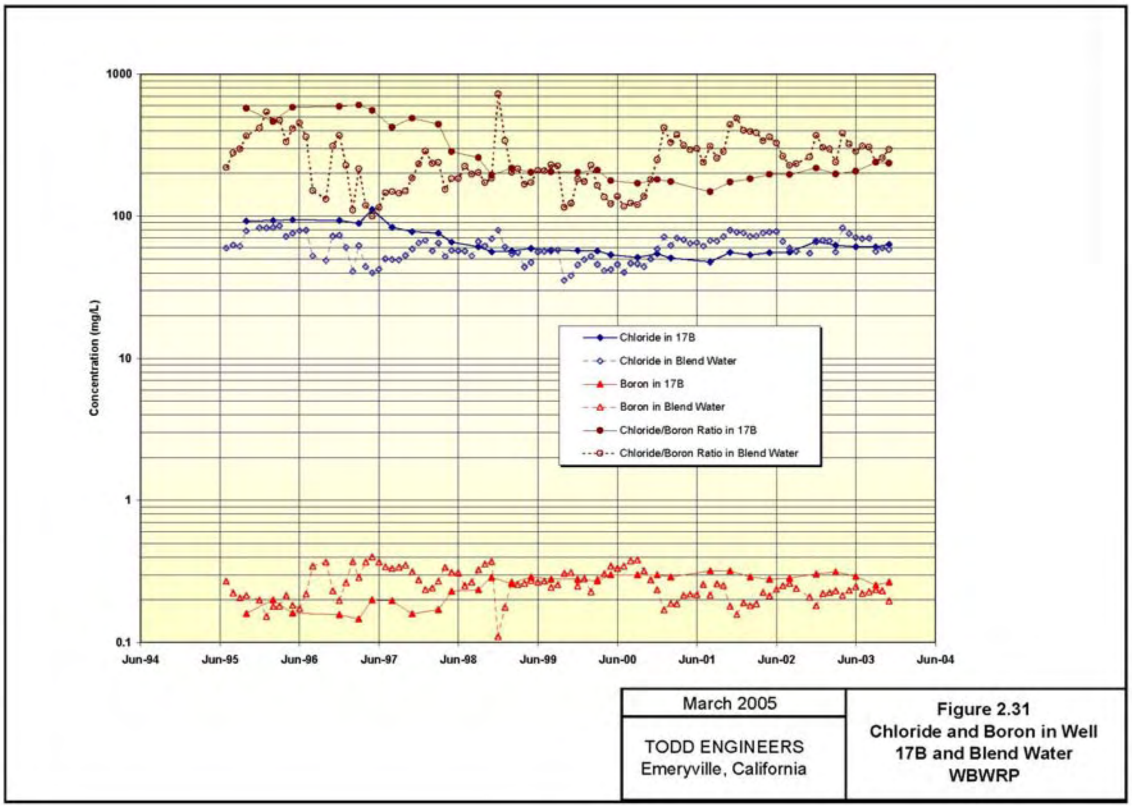


**Figure 2.31. Chloride and Boron in Well 17B and Blend Water, WBWRP.**

*Monitoring Well 690A*

This well is 450 ft west of the barrier and could have shown blend water impacts by mid-1996 (using an estimated transport time of 1.4 ft/day). However, hydraulic gradients and transport west of the barrier are less well known. With seawater flowing inland toward the barrier, migration of blend water to the west could be substantially slower. Well 690A has contained detectable concentrations of NDMA in only three samples and at very low concentrations (average, 3 ng/L).

As shown on the trilinear diagram in Figure 2.33, the well demonstrates an overall water quality that can be characterized as a saline water type (lower right side of central diamond). Although chloride concentrations are not unusually high (110 mg/L), sodium and chloride are the main ions contributing to the overall water chemistry. Other data are consistent with native groundwater plotting in this area of the trilinear diagram.

The water quality type is also observed to be changing significantly through time. Early samples indicate a much higher contribution of sodium and potassium on the cation signature than do later samples (lower left triangle in Figure 2.33). Water type changes systematically over time, as the water quality signature in Well 690A becomes more similar to those of the blend and imported water types, as shown clearly by the changes in overall water type (central diamond in Figure 2.33).

Although this change is more subtle on the anion triangle, the anion signature is perhaps more revealing when correlated to NDMA detections. As noted on the anion signature, early samples are more similar to imported water but move toward blend water over time. The samples that plot closest to the blend water are the same samples that have detected NDMA. More recent samples plot away from the early blend samples and may indicate changing blend water quality over time with lower NDMA concentrations.

*Monitoring Well 1318N*

Well 1318N is located 2866 ft from the barrier and has contained detectable concentrations of NDMA in only one sample (May 2001) at a concentration of 2.6 ng/L. Given an average transport time of a little more than 1.4 ft/day, this NDMA detection could indicate the presence of blend water. However, samples after 2001 did not contain detectable concentrations of NDMA.

When data are plotted on a trilinear diagram, the anion signature appears more similar to that of imported water than to that of blend water (Figure 2.34). It is possible that the NDMA detected in Well 1318N is from imported water, although the interpretation is somewhat speculative, given the variability of the well data signatures. Based on these analyses alone, it is difficult to determine whether the source of the NDMA is blend water. Further, it cannot be determined whether the NDMA concentration in this well has been controlled by mixing, dispersion, degradation, or a combination of these processes.

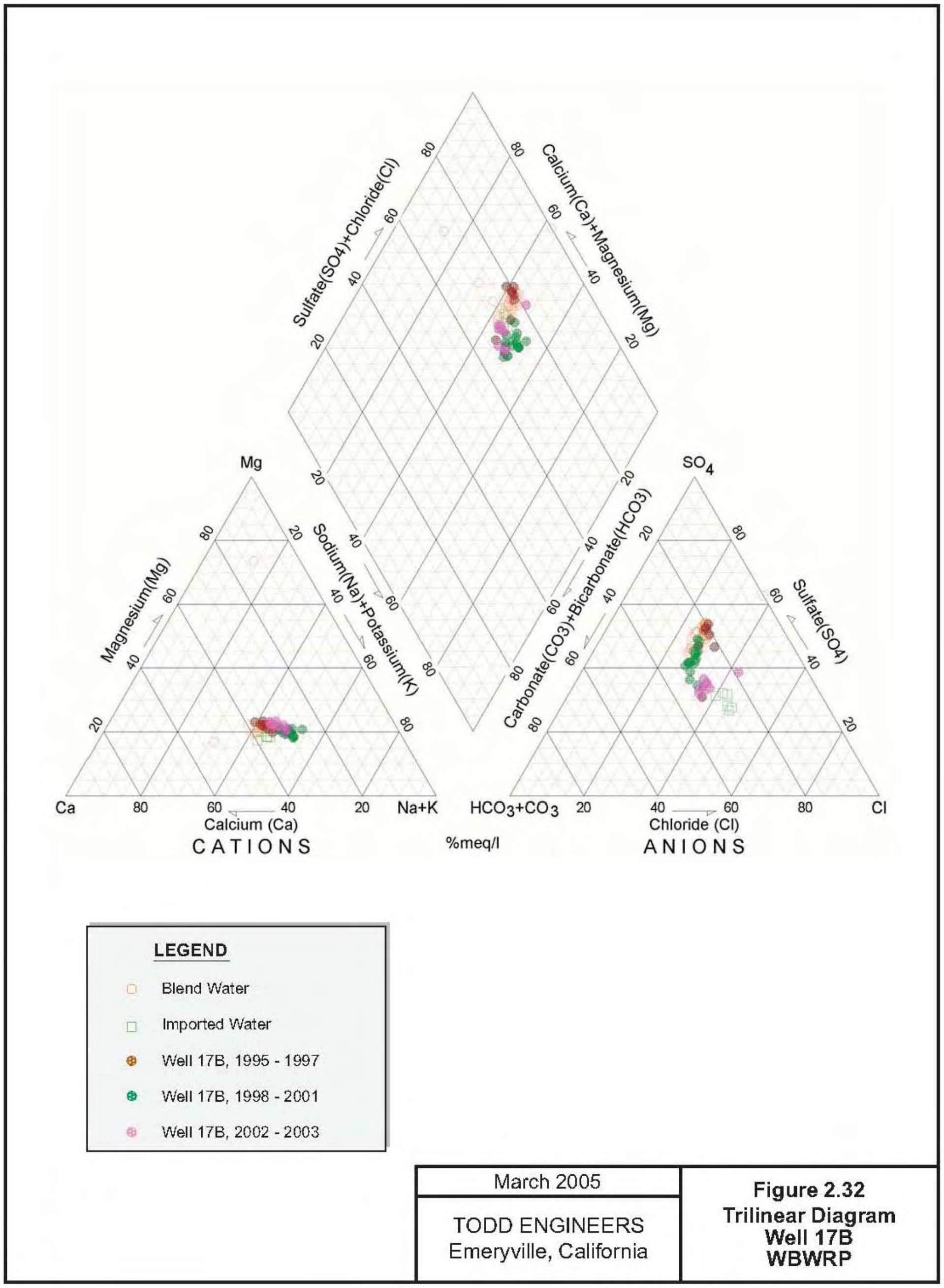


Figure 2.32. Trilinear Diagram, Well 17B, WBWRP.

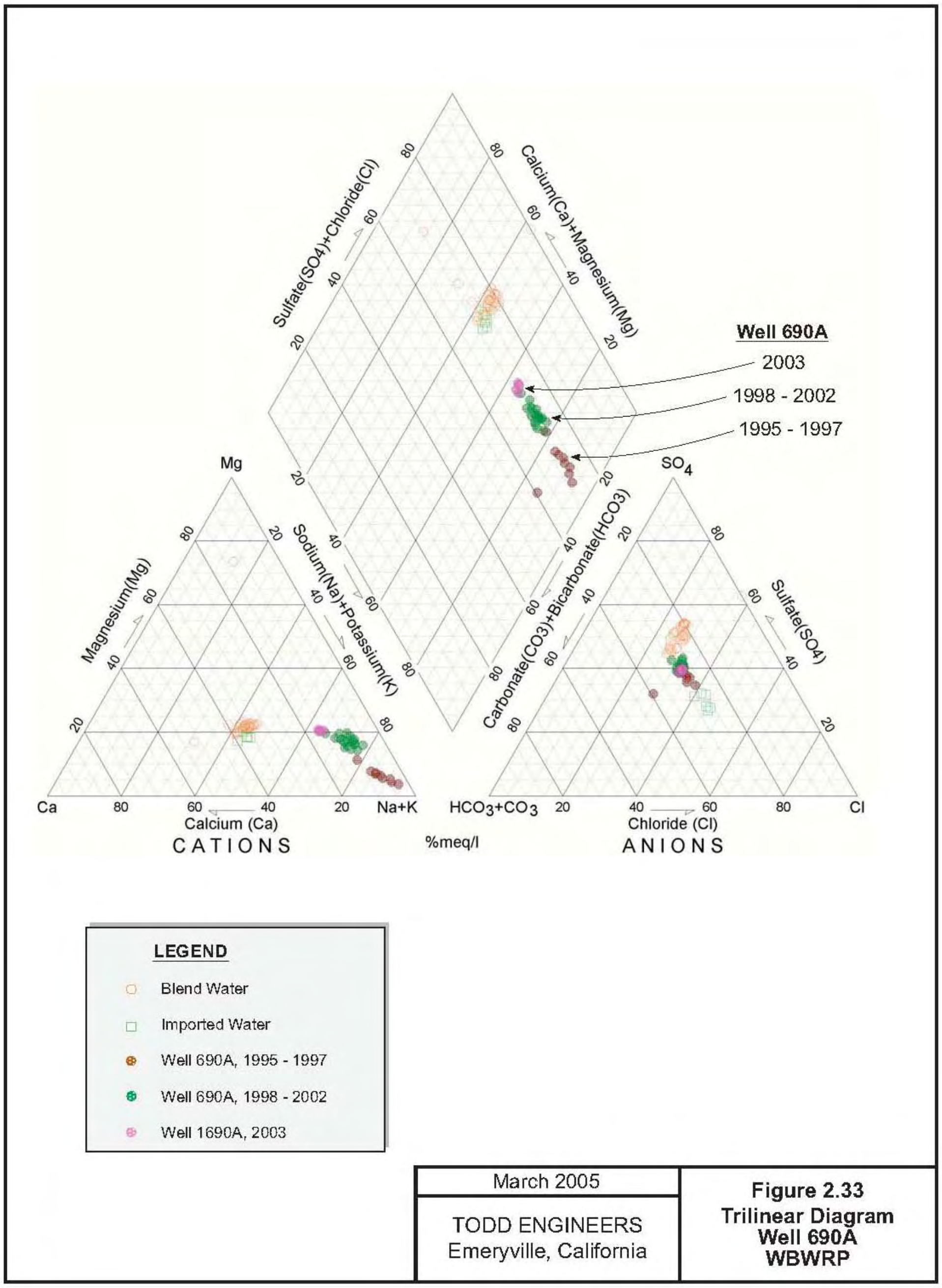


**Figure 2.33. Trilinear Diagram, Well 690A, WBWRP.**

### 2.8.10 NDMA Fate and Transport Summary

- Recycled water blended with imported water has been injected into groundwater along the West Coast Barrier Project since July 1995.
- Both recycled water and imported water (collectively, blend water) have contained detectable concentrations of NDMA, although limited data indicate that concentrations in imported water are much lower.
- From July 2000 through February 2003, NDMA concentrations in blend water ranged from 6 to 1190 ng/L, with an average concentration of 62 ng/L (standard deviation of 115).
- Since March 2001, NDMA concentrations in blend water have been lower and less variable, with an average of 41 ng/L and a standard deviation of 32.
- NDMA concentrations in blend water are a mix of NDMA concentrations in recycled water and low but detectable NDMA concentrations in imported water.
- Transport times for blend water to migrate east (downgradient) from the barrier have been estimated at 0.3 to 1.4 ft/day, based on a 1999 isotopic study.
- Given more complex and variable hydraulic conditions west of the barrier, transport times may be significantly different to the west.
- Using the shorter transport time and June 1995 as the beginning of injection of blend water, NDMA in blend water may have migrated more than 4000 ft downgradient by 2004 (8.5 years at 475 ft/year).
- NDMA has been detected in 8 of 16 monitoring wells at concentrations ranging from 2.0 to 110 ng/L.
- Concentrations were highest near the injection wells and decreased significantly with distance from the barrier.
- Concentrations detected in Well 13B are very similar to concentrations detected in blend water, indicating that neither dispersion nor degradation is causing a significant decrease in NDMA concentrations in this area.
- Well 17B appears to be impacted by blend water based on changes in water chemistry and NDMA detections. However, NDMA concentrations are somewhat lower than would be expected, given the large percentage of blend water estimated to be in the well. This indicates that some degradation of NDMA may be occurring in this area.
- Samples from Well 690A appear to be a mix of blend water and imported water, accounting for the low and sporadic detections of NDMA.
- Samples from Well 1318N appear more similar to imported water than to blend water, indicating that the one NDMA detection in May 2001 may not have originated in blend water.
- Geochemical plots, including trilinear diagrams, are useful in differentiating sources of water in monitoring well samples. In particular, the anion signature appears to be sufficiently different to distinguish between blend water and imported water.

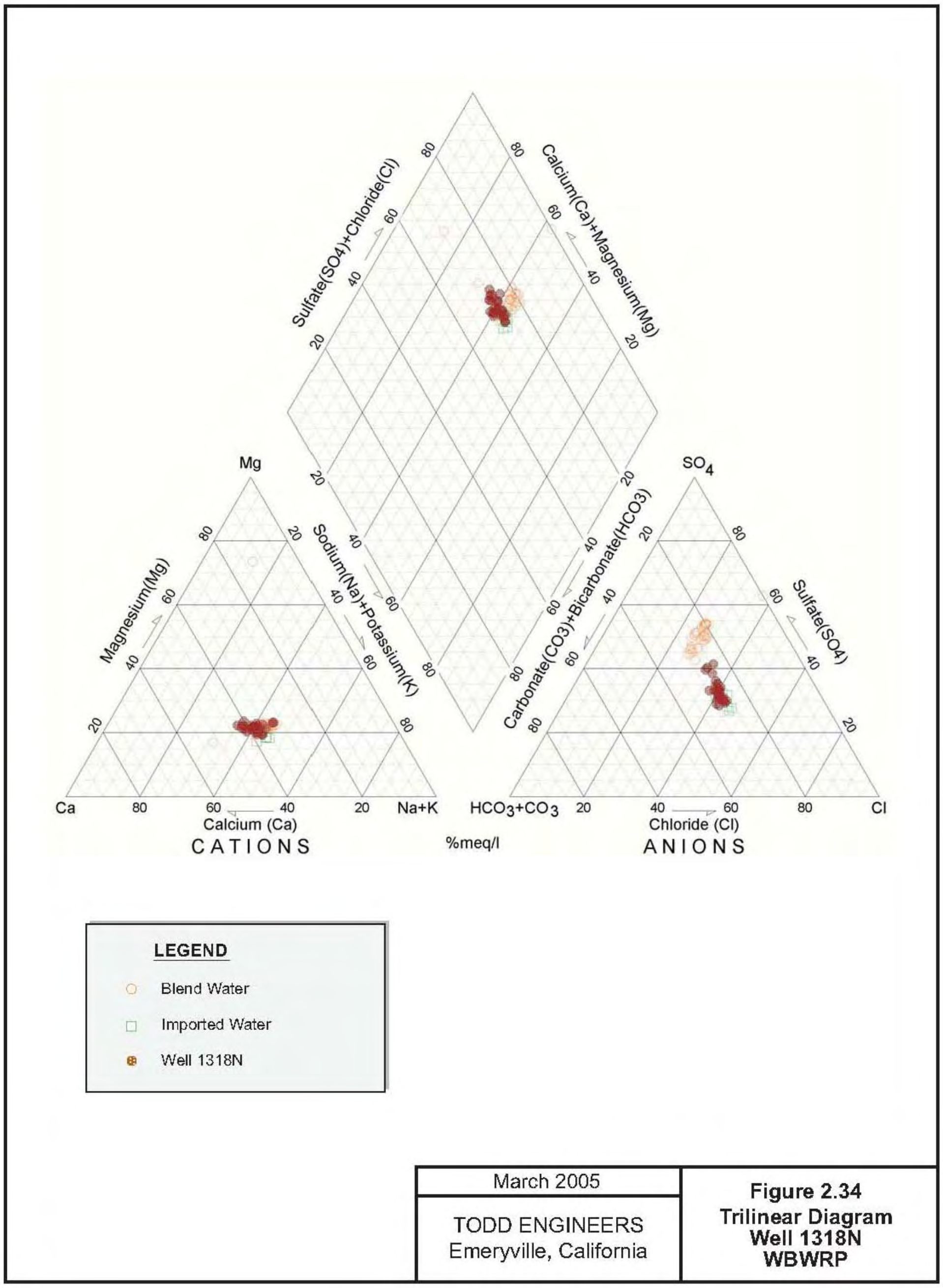


**Figure 2.34. Trilinear Diagram, Well 1318N, WBWRP.**

## 2.9 SANTA CLARA VALLEY WATER DISTRICT WATER RECYCLING

### 2.9.1 Introduction

The Santa Clara Valley Water District (SCVWD) Board of Directors has a policy to expand water recycling in Santa Clara County in order to reduce wastewater effluent discharge to San Francisco Bay and provide a more reliable water supply for the valley residents. The District's targets for water recycling in the county are 5% of total water use by 2010 and 10% of total water use by 2020.

Current recycling programs in Santa Clara County are in the cities of San Jose, Santa Clara, and Milpitas. Recycled water is used to irrigate golf courses, parks, schools, and agricultural lands; to supply industrial processes and cooling towers; and to serve dual plumbing as part of the South Bay Water Recycling Program (SBWRP). Tertiary treated water generated at the San Jose/ Santa Clara Water Pollution Control Plant is the source of recycled water.

Plans are ongoing to expand water recycling into the Coyote Valley and Llagas Subbasin in southern Santa Clara County. Groundwater recharge with recycled water and augmentation of surface water supplies have been evaluated, but to date there is no active surface water augmentation or groundwater recharge taking place in Santa Clara County. The SCVWD recently issued an Advanced Recycled Water Treatment (ARWT) Study, which assessed the feasibility and need of providing higher-quality recycled water than is currently available and/or providing greater volumes of recycled water for a broad variety of uses, including landscape irrigation and agricultural, industrial, and environmental purposes (Black & Veatch et al., 2004).

### 2.9.2 Hydrogeologic Setting

The SBWRP being implemented in Santa Clara County overlies several subbasins in the Santa Clara Valley Groundwater Subbasin. The basin is a structural trough parallel to the northwest trending Coast Ranges and is filled with continental deposits of unconsolidated to semiconsolidated sediments (*Coastal Plain*, 2004). This subbasin is 22 mi long and 15 mi wide and extends from the Coyote Narrows to San Francisco Bay (SCVWD, July 2001).

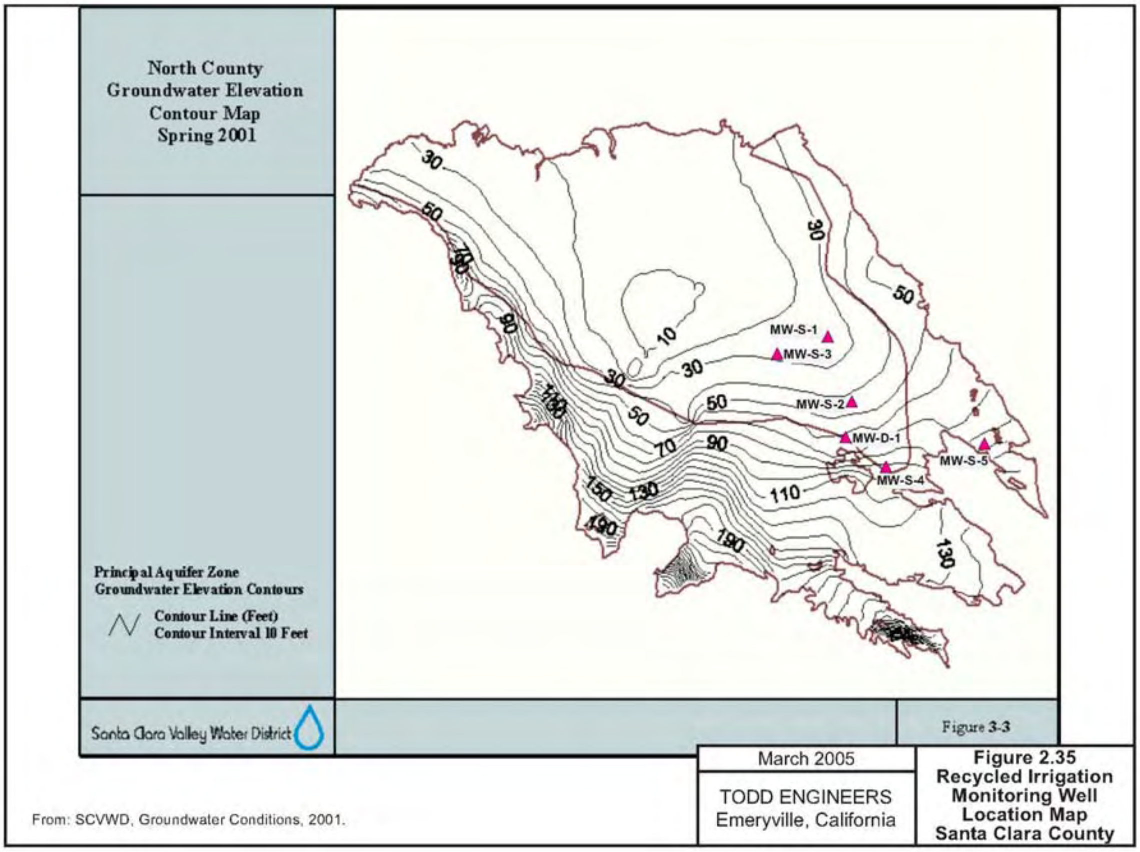
The main aquifer providing water supply in the valley is below a regional aquitard and contains groundwater under confined conditions. Reported well yields are about 1650 gpm (*Coastal Plain*, 2004). The regional aquitard is a thick clay layer that is 150 to 250 ft thick in the northern portion of the subbasin. The aquitard separates the water supply from any surface irrigation and would afford a layer of protection from any constituents in recycled-water irrigation. The level of protection is uncertain, however, because some constituents originating at the surface (e.g., nitrate) have impacted portions of the confined aquifer (Black & Veatch et al., 2004). Groundwater monitoring provides the opportunity to evaluate impacts in the future.

The Santa Clara Valley Confined subbasin is surrounded on the south, east, and west by the Santa Clara Valley Unconfined subbasin. As implied by the name, aquifers in this area are unconfined, and the regional aquitard is thin or absent. This condition exposes the main water supply aquifers to surface recharge and requires additional measures to ensure no adverse impacts from the use of recycled water.

Regionally, groundwater flows northwest to San Francisco Bay. Areas of groundwater pumping control local flow directions in some areas. Figure 2.35 illustrates the flow directions with water level contours for spring 2001 (SCVWD, 2005).

## 2.9.3 Monitoring Data

Since 1997, a network of six monitoring wells has been used to monitor potential impacts of irrigation use of recycled water in Santa Clara County. The six sites where monitoring wells have been installed are shown in Figure 2.35. As shown in the figure, wells are located at selected sites being irrigated with recycled water throughout the county to evaluate groundwater quality. The wells and construction information are presented below in Table 2.10.



From: SCVWD, Groundwater Conditions, 2001.

**Figure 2.35. Recycled Irrigation Monitoring Well Location Map, Santa Clara County.**

**Table 2.10. Santa Clara Valley Recycled Irrigation Monitoring Well Information**

| Well | Screened interval (feet bgs) | Aquifer |
|---|---|---|
| Watson Park MW-S-1 | 20–40 | Upper |
| Columbus Park MW-S-3 | 14–34 | Upper |
| Kelley Park MW-S-2 | 28–48 | Upper |
| Solari Park MW-S-4 | 40–60 | Forebay |
| Evergreen Park MW-S-5 | 36–56 | Forebay |
| Curtner Ave. Right of Way MW-D-1 | 69–89 | Forebay |

Wells were sampled on a quarterly basis for a number of years ending in 2002. The wells were sampled for inorganic constituents, including nitrate, nitrite, chloride, and other general minerals. Initial samples for volatile organic compounds have also been analyzed. The wells have not been tested for NDMA (laboratory analysis sheets were provided by SCVWD; electronic data were not available). Data on anthropogenic indicators or wastewater were also not available.

Laboratory data sheets were reviewed with respect to TDS, chloride, and nitrate, possible recycled-water indicators (Black & Veatch et al., 2004). Concentrations of TDS, chloride, and nitrate (as N) in recycled-water effluent were reported as 727 mg/L (±38), 162 mg/L (±10), and 10.2 mg/L (+2.5), respectively. Monitoring well data for these constituents were entered into an electronic database for further analysis.

Of the six wells in Figure 2.35, only three wells, i.e., MW-D-1, MW-S-2, and MW-S-5, demonstrated increasing trends for any of the constituents from 1997 to 2002 (all available data). Of those three wells, MW-S-2, and MW-D-1 had TDS concentrations higher than measured in effluent; therefore, increasing trends in those two wells are not likely the result of recycled-water irrigation. For the third well with increasing trends, only a slight increase in TDS and chloride is apparent from the data. Without additional details on background water quality data and site-specific hydrogeologic data at each project area, it is difficult to make generalizations about specific water quality impacts from recycled water using only the inorganic data provided.

Water quality data may also be available in the vicinity of other SBWRP projects where dedicated monitoring wells have not been installed. One unmonitored recycled-water project at the San Jose Municipal Golf Course with nearby wells is shown in Figure 2.36. Recycled water has been used for irrigation at the golf course since June 1997 (SCVWD, personal communication). Approximately six wells within about 1.5 mi were located. Wells have not been monitored for NDMA.

Although their location is suitable, it appears that available wells may be inappropriate for monitoring potential impacts from the golf course irrigation project. Wells monitored by SCVWD and other entities may not be appropriately constructed to assess impacts to shallow groundwater. In addition, these wells seem too far from the site. Given the 7 years since irrigation began, recycled water would not be expected to have reached most of these wells, even if wells were properly located and appropriately screened. Therefore, it is unlikely that these wells would provide sufficient data to evaluate potential impacts from recycled water on local groundwater.

Recognizing the importance of characterizing background water quality, SCVWD supported a well sampling program for use in the ARWT Study (Black & Veatch, 2004). Effluent, surface water, and groundwater quality were tested at 10 locations. Three rounds of sampling over 10 months were conducted except for the Palo Alto Regional Water Quality Control Plant effluent, which was sampled twice. A number of parameters were analyzed, including NDMA. The locations and water type are listed in Table 2.11.

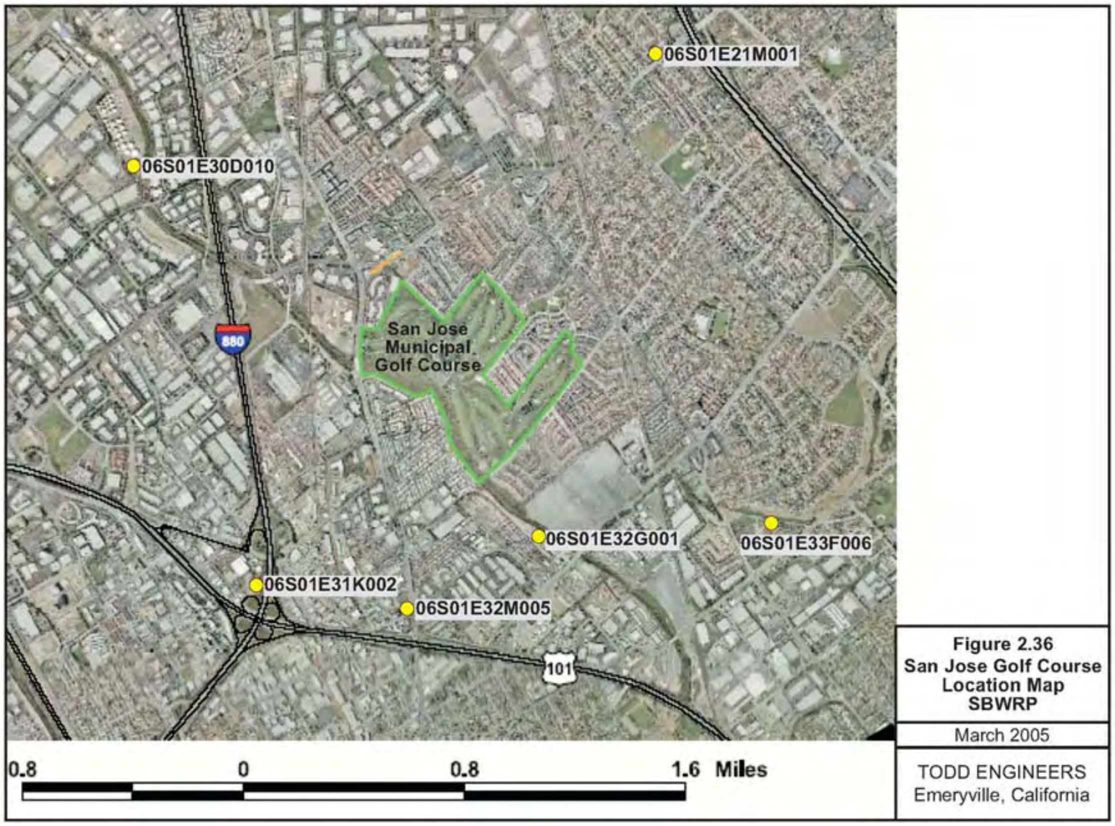


Figure 2.36. San Jose Golf Course Location Map, SBWRP.

**Table 2.11. ARWT Water Quality Sampling - SBWRP[1]**

| Location | Water type | Baseline NDMA sampling results (avg no. of ng/L) |
|---|---|---|
| Anderson Reservoir | Surface water | ND |
| Coyote Creek Outdoor Classroom Shallow Well (screened 60–70 ft bgs) | Shallow groundwater | ND |
| Coyote Creek Outdoor Classroom Deep Well (screened 405–425 ft bgs) | Deep groundwater | ND |
| Coyote Valley Well<br>(screened 100 ft bgs) | Unconfined groundwater | ND |
| Gilroy Shallow Well<br>(screened 95–100 ft bgs) | Shallow groundwater | ND |
| Gilroy Deep Well<br>(screened 135–170 ft bgs) | Deep groundwater | ND |
| Sunnyvale Water Pollution Control Plant | Effluent | 65 |
| San Jose/Santa Clara Water Pollution Control Plant | Effluent | 29 |
| South County Regional Water Authority Gilroy Plant | Effluent | 3.5 |
| Palo Alto Regional Water Quality Control Plant | Effluent | 375*<br>11 |

[1] ND, NDMA not detected;
*, elevated value thought to be associated with a temporary discharge.

NDMA was not detected in any of the surface water or groundwater samples. However, it is noted that the surface water and groundwater sampling locations were not selected to represent locations that would likely be impacted by existing wastewater application but rather to provide baseline information for the ARWT Study analyses.

NDMA was detected in effluent from all four wastewater treatment plants (WWTPs). The average results of the effluent samples analyzed for NDMA were 3.5 ng/L in the South County Regional Water Authority Gilroy Plant, 29 ng/L in the San Jose/Santa Clara Water Pollution Control Plant, 65 ng/L in the Sunnyvale Water Pollution Control Plant, and 375 ng/L in the Palo Alto Regional Water Quality Control Plant. Previous NDMA sampling of effluent from the Palo Alto Plant by the city never detected NDMA above 11 ng/L, and the elevated level detected during the ARWT Study was thought to be the result of a temporary discharge from an industrial source. The San Jose/Santa Clara Water Pollution Control Plant is the source of recycled water applied and used in the Santa Clara Valley recycling program.

### 2.9.4 Summary and Recommendations

- Recycled water has been used for irrigation projects since 1997. Water is supplied by the San Jose/Santa Clara Water Pollution Control Plant, which contained 29 ng of NDMA/L.

- Monitoring wells at the recycled-water sites have not been analyzed for NDMA.
- A trend analysis for TDS, chloride, and nitrate concentrations in monitoring wells indicated only one well with an increase in TDS and chloride concentrations at levels that could be the result of recycled water. However, without additional analyses of background water quality, no conclusions about the impacts from recycled water can be made based on these data alone.
- The objective of ARWT testing for NDMA in groundwater was to characterize background water quality. Well locations were not selected to evaluate NDMA from recycled-water projects.
- Given the relatively low concentration of NDMA in effluent, the protection of a regional aquitard beneath many of the existing irrigation sites, and the possible attenuation of NDMA on the ground surface and vadose zone, it is unlikely that elevated levels of NDMA persist in downgradient aquifers beneath these selected sites. Additional research may be needed to assess the fate of NDMA in the unconfined areas of the basin where direct pathways to water supply aquifers exist.

## 2.10 FATE AND TRANSPORT OF NDMA IN GROUNDWATER SUMMARY AND CONCLUSIONS

An examination of field data from six sites where NDMA has been released allows for the comparison of NDMA occurrence from site to site. In consideration of the sites as a whole, additional observations can be made about the fate and transport of NDMA in groundwater.

The summary table below lists general characteristics of NDMA in source water and resulting impacts to groundwater at each site. The “plume length” column generally lists the maximum distance of downgradient NDMA detections in groundwater; three of the sites, including the MFRP, West Coast Barrier, and South Bay Water Recycling Project, do not appear to have a definable plume of NDMA concentrations in groundwater. In general, NDMA data in source water are available from only about 1999 or 2000, limiting the level of confidence of NDMA source water estimates, especially for the earlier releases.

Based on the field data at the selected sites, the following observations are made with respect to the fate and transport of NDMA in groundwater:

- Most of the plume lengths are consistent with independent estimates of groundwater flow velocities, indicating that NDMA is not being sorbed or otherwise retarded with respect to groundwater flow.
- A general correlation can be observed between the NDMA concentration in source water and the persistence of elevated NDMA concentrations in downgradient groundwater.
- In areas where NDMA was released from a relatively small source area, plumes appear narrow and well defined with steep concentration gradients. This observation indicates that dispersion is not a major factor in most of the NDMA plumes analyzed.
- At many sites, NDMA mass is spread laterally and vertically by induced gradients from pumping wells. This appears to be the major mechanism for spreading NDMA throughout the aquifer.
- At several sites, relatively high concentrations of NDMA persist downgradient for several miles, indicating that NDMA is not being significantly transformed or removed from the system.
- Since mass is spread throughout the aquifer at most sites, it is difficult to determine whether degradation is removing a significant mass of NDMA from the groundwater

system. At one site, degradation is inferred to be significant in one well while not significant in another well at the same site (West Coast Barrier Project).

- Changes in the groundwater system redox are expected, especially in areas where oxygenated water is injected into an otherwise anaerobic aquifer. Therefore, biodegradation may be occurring in some parts of the aquifer and not in others.
- Biodegradation in the groundwater system, if occurring, does not appear to have decreased NDMA concentrations below levels of concern at most sites.

**Table 2.12. NDMA Site Comparisons**

| Site | Source water | NDMA in source water (ng/L) | Estimated release date | NDMA plume length (ft) |
|---|---|---|---|---|
| San Gabriel Valley Baldwin Park OU | Monitoring well in source area[1] | 3670 | 1943 | 42,000 |
| Rancho Cordova Aerospace Facility | Treatment plant effluent | 250 | 1983[2] | >5000 |
| MFRP | Recharge water | 75[3] | 1962 | 5000[5] |
| Talbert Barrier Injection Project | Injection blend water | 65[4] | 1976 | 10,200 |
| West Coast Barrier Injection Project | Injection blend water | 62 | 1995 | 2866[5] |
| South Bay Water Recycling Project | Treatment plant effluent | 29 | 1997 | Unknown |

[1] Source water unknown; current well average likely underestimates NDMA concentration.
[2] Release date refers to western plume only.
[3] Average concentration of all recharge water samples; effluent concentrations are higher.
[4] Average data before NDMA treatment.
[5] No discernible plume; maximum distance downgradient that NDMA has been detected.

# CHAPTER 3

# FATE AND TRANSPORT OF NDMA AND NDMA PRECURSORS

The fate and transport of NDMA during landscape irrigation with wastewater effluent and during aquifer recharge by surface spreading of wastewater effluent or direct injection of effluent from advanced WWTPs will be greatly affected by processes that result in NDMA retardation or degradation. A review of the chemical properties of NDMA and previous research (Mitch et al., 2003a) indicates that biotransformation and sorption to soil and aquifer particles are the most important processes affecting NDMA fate and transport. While the biotransformation of NDMA has been reported in several previous studies with soil microcosms, little information is available on the organisms responsible for NDMA degradation or the pathways of NDMA biotransformation. NDMA sorption onto soil particles and aquifer solids also has been reported, but little information is available on the importance of this process under conditions likely to be encountered or employed during landscape irrigation.

In addition to NDMA, municipal wastewater effluents contain elevated concentrations of NDMA precursors. NDMA precursors are not expected to pose a problem for advanced treatment plants that practice direct injection because the NDMA precursors in wastewater effluent are effectively removed by RO (Mitch and Sedlak, 2004). When the NDMA precursors in wastewater effluent are subject to disinfection with chloramines, or when chloramines are used as the residual disinfectant in a drinking-water distribution system, concentrations of NDMA in excess of the CDHS NL of 10 ng/L may be formed (Mitch et al., 2003b). Some NDMA may also be produced when free chlorine is used as the only disinfectant, but the concentrations are unlikely to exceed the NL. Because NDMA precursors could also pose a concern for drinking-water suppliers in locations where landscape irrigation or groundwater recharge by surface spreading is practiced, information is needed on the fate of NDMA precursors in the aquatic environment.

To obtain a better understanding of the effect of biotransformation and sorption on the fate and transport of NDMA and NDMA precursors, a series of experiments was conducted under controlled laboratory conditions. The first set of experiments, reported in section 3.1, was aimed at characterization of NDMA biodegradation by pure strains of bacteria. These experiments were complemented by studies designed to assess NDMA sorption and biotransformation by mixed bacterial cultures under conditions encountered in soils where landscape irrigation is practiced (section 3.2). To assess the stability of NDMA precursors in the presence of bacteria, a series of experiments was performed by exposing NDMA precursors from municipal WWTPs to a mixed bacterial culture (section 3.3).

## 3.1 BIOTRANSFORMATION OF NDMA

To assess the potential for microbes to degrade NDMA and to determine which enzymes are responsible for NDMA degradation, we studied NDMA-containing solutions to pure bacterial cultures. Our research focused on improving our understanding of the mechanisms for NDMA degradation, the pathways of the reaction, capabilities of strains to degrade NDMA at environmentally relevant concentrations, and the kinetics of degradation.

### 3.1.1 Materials and Methods

The variety of bacterial strains used in our research necessitated culture-specific modifications of growth and maintenance conditions; however, the conditions were kept as similar as possible to facilitate interspecies comparisons. The wild-type strains used in this study were grown on minimal basal salts medium (Deeb et al., 2002), referred to hereafter as BSM. For toluene induction, toluene was supplied in the vapor phase by adding 30 μL of toluene to a secondary container within the growth flask. Propane and methane were supplied by injecting 30% (v/v) of the gas into the sealed liquid culture flasks. Tryptic soy broth was used as a rich medium for experiments designed to promote cellular growth while not inducing for a specific oxygenase enzyme. The *Escherichia coli* strains containing the plasmids were grown in LB (Luria–Bertani; Becton–Dickinson, Sparks, MD) medium supplemented with kanamycin at 100 mg/L. Cells were incubated in sealed 500-mL or 1000-mL clear flasks containing 100 or 200 mL of BSM, respectively, and were harvested in the late exponential phase of growth (optical density at 600 nm [$OD_{600}$] between 0.8 and 1.4).

All cells were incubated aerobically with shaking at 150 rpm and 30 °C, and standard microbial aseptic techniques were used throughout. Cellular mass was quantified by using a Pierce Coomassie Plus Protein Assay Kit (Rockford, IL) with digestion accomplished by bead-beating the cells for 2 min followed by boiling for 15 min. To ensure cellular purity, experiments were begun either from a single, large colony or from liquid medium containing an uncontaminated strain. Samples of liquid suspension were streaked onto LB plates to verify colony purity. Most results were performed in duplicate, and all were independently repeated from the original cultures to ensure reproducibility.

At the beginning of each experiment, cells were harvested by centrifugation at 15,000 × *g* for 5 min followed by suspension of the cellular pellet in fresh BSM. This process was repeated a total of three times to ensure that the experimental medium was devoid of unintended substrates. The concentration of the resultant suspension was adjusted with BSM to a strain-specific target density ($OD_{600}$ between 0.1 and 1.8) in order to accurately quantify the degradation rate.

In studies that involved acetylene, a rapid intermediate incubation of 6% acetylene gas was followed by purging the bottles with nitrogen gas, at which point the cells were transferred to the experimental bottles. In all experiments, NDMA (200 μg/L) was added to the bottles at the same time as the cellular addition. The addition of fixed concentrations of NDMA to BSM was used to generate both standards and abiotic controls. Time–course experiments were conducted by removing 2 mL of culture solution from incubations at each time point of interest. Unless otherwise stated, all incubations were performed at 30 °C and 150 rpm to ensure viable cellular populations, enzyme activity, and phase partitioning.

For studies involving degradation from an initial concentration of 200 μg/L, a 2-mL sample of culture solution was removed from incubation bottles and combined with an equal volume of methylene chloride in a 20-mL scintillation vial. This mixture was shaken for 10 min in a cellular incubator (150 rpm and 30 °C). Then approximately 1 mL of the methylene chloride fraction was transferred to a crimp-sealed vial for analysis. Both active and control vials were extracted simultaneously. The detection limit using this rapid liquid–liquid extraction was approximately 5 μg/L. For cellular extractions involving lower concentrations of NDMA, extraction and analysis methods were identical to those described in section 3.3.

Methylene chloride extracts containing NDMA were analyzed by using the procedures of Mitch and Sedlak (2002). Analysis was performed on a Varian CP-3900 gas chromatograph coupled to a Saturn ion trap 2100T MS/MS containing an HP-5MS capillary column (30 m [length] by 0.25 mm [i.d.] by 1 µm [thickness] [JW Scientific]). An autosampler was employed for splitless injections of 2 µL with an injection port temperature of 200 °C, a transfer line temperature of 260 °C, and a trap temperature of 150 °C. Gas chromatography (GC) temperature conditions were as follows: 35 °C (hold time, 1 min) ramping at 10 °C/min to 70 °C, then ramping at 2 °C/min to 83 °C, followed by ramping at 10 °C/min to 220 °C and holding for 2.4 min. Helium carrier gas (99.999% purity) was maintained at 1.2 mL/min. Tandem mass spectrometry was performed by chemical ionization with methanol. The emission current was 60 µA, excitation amplitude 0.32 V, and multiplier offset 100 V. NDMA was quantified by using the 44 and 47 daughter ions. The retention time was 7.1 min.

Nitrite was quantified by using a colorimetric method adapted from Parsons et al. (1984) in which the nitrite in the cellular suspension is reacted with sulfanilamide and *N*-(1-naphthyl)-ethylenediamine to form an azo dye. The resultant pink dye was quantified at 540 nm.

Formaldehyde was quantified by adapting NIOSH method 3500 (Cares, 1968; NIOSH, 1994) for water systems. For this method, the formaldehyde was fixed with a sodium bisulfite solution to eliminate chemical interference and then reacted with chromotrophic acid. The solution was then reacted with concentrated sulfuric acid to yield a purple adduct that was quantified at 580 nm.

A colorimetric assay for monooxygenase activity was adapted from Brusseau et al. (1990). A 5-mL aliquot of cellular suspension was incubated at 150 rpm and 30 °C for 30 min in the presence of 1 mg of naphthalene crystals to facilitate the potential oxidation to naphthol. A 200-µL aliquot of 0.2% (w/v) tetrazotized *o*-dianisidine was then added to the suspension. The resultant naphthol-diazo complex was a purple liquid whose absorbance can be measured at 528 nm in order to quantify naphthalene oxidation as a surrogate for monooxygenase activity.

### 3.1.2 Bacteria and Enzymes Capable of NDMA Mineralization

We identified five strains of common soil microbes capable of degrading NDMA, and the rates of NDMA degradation were measured when different substrates were supplied to the bacteria (Table 3.1). Not only have we shown that it is possible for these bacteria to degrade NDMA, we also identified the responsible enzymatic systems. Four of the strains that can degrade NDMA express genes for monooxygenase enzymes, while the enzyme in the fifth strain of NDMA-degrading bacteria is unknown but could also be a monooxygenase. Conversely, bacteria that did not express for monooxygenase enzymes had no observable capability for the biodegradation of NDMA. Interestingly, cells of *Rhodococcus sp.* RR1 induced on propane as a growth substrate possessed an activity that was at least 10 times faster than that of cells induced on soy broth. This finding is discussed in more detail in section 3.1.4.

Four additional lines of evidence support our hypothesis that NDMA biotransformation involves monooxygenase enzymes.

- NDMA degradation ceases when NDMA-degrading bacteria are grown in the presence of acetylene gas. Acetylene gas is known to prevent the induction of monooxygenase enzymes.

**Table 3.1. Biodegradation Summary of Selected Common Soil Bacteria**[1]

| **Bacterial Strain** | **Induced Oxygenase** | **Substrate** | $k_{NDMA}$ **[ng/mg/min]** |
|---|---|---|---|
| *Mycobacterium vaccae* JOB-5 | propane monooxygenase | propane | 100 |
| *Rhodococcus sp.* RR1 | unknown | propane | 400 |
| *Rhodococcus sp.* RR1 | unknown | soy broth | 10 |
| *Methylosinus trichosporium* OB3b | soluble methane monooxygenase | methane | 3 |
| *Methylosinus trichosporium* OB3b | particulate methane monooxy | methane | 0 |
| *Pseudomonas mendocina* KR1 | tol 4-monooxygenase (T4MO) | toluene | 5 |
| Recombinant *E. coli* TG1(T4MO) | tol 4-monooxygenase (T4MO) | LB | Observed |
| *Ralstonia pickettii* PKO1 | tol 4-monooxygenase (TpMO) | toluene | 1 |
| Recombinant *E. coli* TG1(TpMO) | tol 4-monooxygenase (TpMO) | LB | Observed |
| *Burkholderia cepacia* G4 | tol 2-monooxygenase | toluene | 0 |
| Recombinant *E. coli* TG1(T2MO) | tol 2-monooxygenase | LB | 0 |
| *Pseudomonas putida* mt-2 | tol side-chain monooxygenase | toluene | 0 |
| *Pseudomonas putida* F1 | tol 2,3 dioxygenase | toluene | 0 |
| *Pseudomonas flourescens* CFS215 | tol 2,3 dioxygenase | toluene | 0 |
| *Escherichia coli* pCR 2.1-TOPO | no oxygenase | soy broth | 0 |

- NDMA degradation deactivation ceases when NDMA-degrading *Methylosinus trichosporium* OB3b is grown in the presence of 4 μM $Cu^{2+}$. In the presence of these elevated concentrations of copper the particulate methane monooxygenase is induced rather than the soluble methane monooxygenase enzyme.
- NDMA degradation rates are correlated with results from the napthol-azo colorimetric assay, which detects the presence of monooxygenase enzymes.
- NDMA is degraded by recombinant *E. coli* strains TG1 (T4MO) and TG1 (TpMO) (Table 3.1). These strains of bacteria have been engineered to contain toluene monooxygenase enzymes derived from strains *Pseudomonas mendocina* KR1 and *Ralstonia pickettii* PKO1.

This last line of evidence was viewed as the most compelling for the involvement of monooxygenase enzymes because *E. coli* bacteria, which normally do not degrade NDMA, achieved activity when constitutively regulated plasmids containing the toluene monooxygenases were introduced into the bacterium (Fishman et al., 2004; Tao et al., 2004). This approach also enabled an interspecies comparison of enzyme affinity. Our results demonstrated that, while the T4MO and TpMO (formerly T3MO) could biodegrade NDMA, the T2MO was unable to degrade NDMA. Not only did this experiment support the involvement of monooxygenases in NDMA biodegradation, it demonstrated marked differences in substrate affinity between these different enzymes.

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[1] For these experiments, the growth substrate was removed prior to NDMA exposure to encourage oxygenase activity. Reported rates were for an initial NDMA concentration of 200 mg/L and are reported as number of nanograms of NDMA/milligrams of cellular protein/minute.

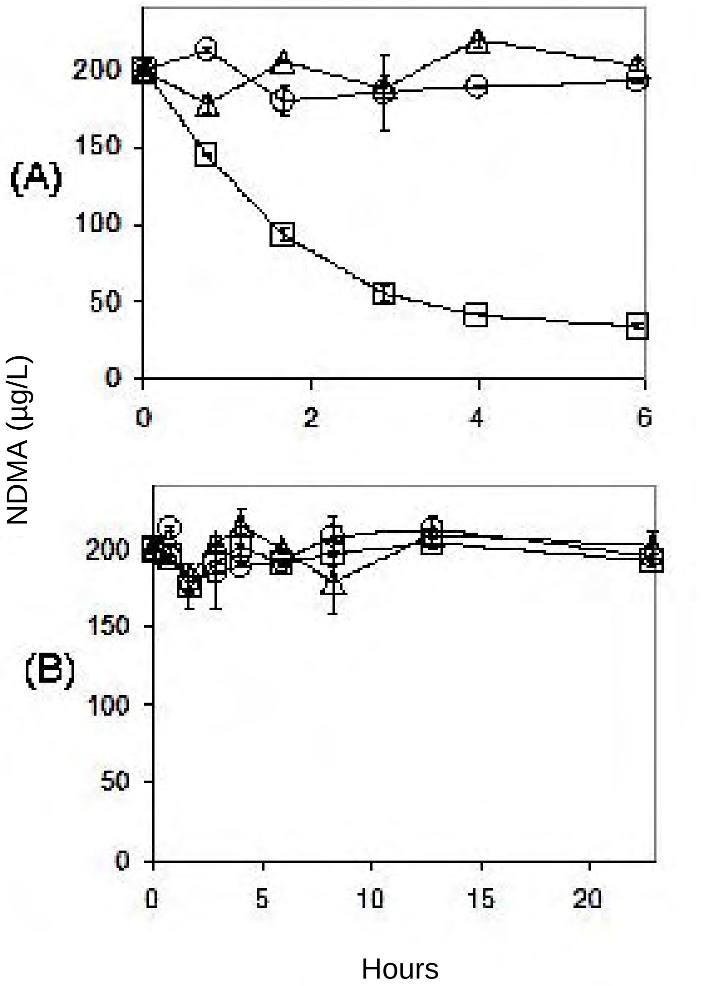


**Figure 3.1. Degradation of NDMA by *M. trichosporium* OB3b.**
Protein (A) (270 mg/L) grown on methane in the absence of copper to induce sMMO and (B) (318 mg/L) grown on methane in the presence of copper to induce pMMO. Key: hollow square = active bacteria; hollow triangle = active bacteria exposed briefly to acetylene gas; hollow circle = abiotic controls. Experiments were conducted in duplicate bottles with error bars depicting data range. In some cases, the error bars are smaller than the symbols.

Our research describing the capability of axenic strains and their expressed monooxygenase enzymes to biodegrade NDMA has been accepted for publication in *Biotechnology and Bioengineering* (Sharp et al., 2005). We expect that the research will trigger further research and interest in this area.

Despite vigorous attempts, we have been unable to sustain growth of any strains on NDMA. We had hoped that our observation of a convex rather than concave degradation curve (as shown here for strain OB3b) exhibited by strain RR1 after induction on soy broth implied that the cells could derive energy from NDMA biodegradation, as such a curve usually suggests an increased rate with time. However, it appears that any energy generated from NDMA biodegradation is small and difficult to sustain over a period of days and that, if growth does occur, it is too anemic to effectively quantify. We have also attempted to grow the closest genetically related and functionally analogous *R. ruber* strain (identified by 16s rDNA GenBank sequence) with similar negative results. We also failed to grow a mixed culture of bacteria on NDMA by using soil samples collected from the landscape irrigation site described in Chapter 4.

Our inability to grow bacteria on NDMA is consistent with results from previous researchers (Kaplan and Kaplan, 1985; Gunnison et al., 2000). Furthermore, though growth of bacteria on NDMA would have provided further evidence of the ability of specific strains or mixed culture to degrade NDMA, it is probably of little relevance to soil and groundwater systems where water reuse is practiced, because the concentrations of NDMA in such systems are unlikely to be high enough to sustain metabolic growth of bacteria on NDMA. Thus, a system involving cometabolic degradation appears to be a more realistic model of the processes that lead to biodegradation of NDMA in systems of interest to practitioners of water reuse.

### 3.1.3 Mechanisms of NDMA Removal by Monooxygenase Enzymes

As stated in section 3.1.2, a propane-grown *Rhodococcus sp.* RR1 strain degrades NDMA at a rate of 400 ng/mg of protein/min (Figure 3.2), which is 40 times higher than the rate for our constitutively expressing soy-grown cells from the same strain (Sharp et al., 2005) and is over 100 times higher than the previously reported rate for *M. trichosporium* OB3b (Sharp et al., 2005; Yoshinari and Shafer, 1990). Importantly, this and all of our experiments summarized in Table 3.1 were conducted at concentrations (initial NDMA concentrations of 200 µg/L) that are closer to environmentally relevant levels than were the levels cited in any of the previous studies in the scientific literature (e.g., initial NDMA concentrations of 2,200 to 740,000 µg/L were used [Rowland and Grasso, 1975; Yoshinari and Shafer, 1990]). In addition, the extent of NDMA degradation reported in our studies ranged from 40% to greater than 99%, compared to less than 4% reported previously (Rowland and Grasso, 1975; Yoshinari and Shafer, 1990). Therefore, our studies and particularly *Rhodococcus sp.* RR1 and its putative PMO represent a more reasonable model for NDMA degradation than do the previously studied strains. We hope to pursue this finding further through collaboration with Professor Thomas Wood at the University of Connecticut to clone this putative propane monooxygenase into *E. coli* in order to enhance our ability to study this potent enzyme.

It is our hope that cloning the enzyme will enable us to answer questions about this putative monooxygenase that we had originally hoped to accomplish by isolating the protein. Despite numerous attempts at protein isolation with techniques including cellular lysis (French press, sonication, and lysozyme) and incubation assays (energy sources, osmolarity, pH, and water hardness), we have not been able to detect NDMA enzyme activity in protein extractions subsequent to cellular lysis. Possible explanations are that the enzyme is a multicomponent, soluble enzyme or that the protein is membrane bound. Previously characterized monooxygenase enzymes that we have identified as cometabolic NDMA biodegrading proteins were found to be solubilized in the cellular cytoplasm and shared analogous $(\alpha\beta\gamma)_2$ protein structures. It is our hypothesis that the *Rhodococcus sp*. RR1 strain (in which NDMA degradation is catalyzed by an unknown enzyme) contains a structurally analogous, multicomponent enzyme found in the soluble protein fraction, but this view cannot be verified without protein purification.

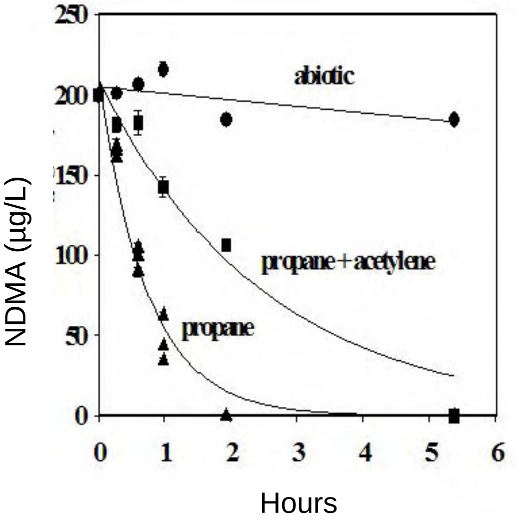


**Figure 3.2. NDMA Degradation with Propane-Grown Cells.**
Propane (20% by volume) was added to the headspace of *Rhodococcus sp.* strain RR1 to induce expression of PMO. Note that the addition of acetylene reduces the NDMA degradation rate, which suggests the presence of a monooxygenase.

The finding of NDMA biodegradation by propane-grown RR1 bacteria also has potential for application to hazardous waste sites, where addition of propane might be used to enhance the rate of biodegradation of NDMA. Our preliminary results in this direction are promising, as a propane enrichment cultured from soil slurries derived from Jay Gan’s irrigated turf plots at UC Riverside demonstrated the capability to biodegrade NDMA. Furthermore, the expression of a constitutive (always active regardless of growth conditions) enzyme in strain RR1 is promising because it suggests that NDMA-degrading enzymes may be naturally generated in the subsurface by indigenous bacteria. Thus, additional research may help us to identify conditions in landscape irrigation and groundwater recharge systems that are conducive to NDMA biodegradation.

In addition to our identification of an enzyme that is likely to play an important role in NDMA biodegradation, we investigated the capabilities of bacteria to biodegrade NDMA at concentrations that are relevant to landscape irrigation and groundwater recharge systems. To this end, experiments were conducted to assess the ability of monooxygenase enzymes to degrade low concentrations of NDMA. Our results suggest that, while the fastest strains can remove over 95% of the NDMA when starting at a concentration of 2000 ng of NDMA/L, achieving the CDHS NL of 10 ng/L purely through biological activity can be challenging. Final NDMA values measured in these studies were 53 ± 6 ng/L for the *Rhodococcus* and 88 ± 1 ng/L for the *Mycobacterium*. A more promising result for the attainment of CDHS NL occurred when a more concentrated cellular slurry (>100 mg/L) of the *Rhodococcus* strain was incubated overnight in the presence of 200 ng of NDMA/L. In this study the final NDMA concentration was close to 10 ng/L; however, a >50% loss of NDMA was observed in the controls, and therefore these data are inconclusive. We have not yet had the opportunity to quantify the rate and extent of NDMA degradation under these environmentally relevant NDMA conditions when strain RR1 is grown on propane. However, we expect that this strain will degrade NDMA under these conditions as well as or better than when it is grown on soy broth. For this reason, we believe that it has the greatest chance of achieving NDMA removal to the CDHS NL.

### 3.1.4 Biodegradation Rates and Pathway

Rates of NDMA degradation by the bacteria in our studies have been calculated (Table 3.1). These rates ranged from a low of 1 ng of NDMA/mg of cellular protein/min to a high of 400 ng/mg/min when the cells were exposed to an initial concentration of 200 μg of NDMA/L.

On the basis of previous research with monooxygenase enzymes and studies of NDMA metabolism by P-450 systems in mammals, we propose a degradation pathway for NDMA (Figure 3.3). The first step of this reaction is expected to involve hydroxylation of one of the methyl carbons by the monooxygenase enzyme (Kroeger-Koepke et al., 1981). The unstable alkyl nitrosamine then undergoes a fragmentation reaction to form formaldehyde and a diazonium ion, which then decays to nitrogen gas and a methylated nucleophile (Carey, 1992). In addition to this hydroxylation pathway (Kroeger-Koepke et al., 1981), previous studies have shown that P-450 enzymes can mediate a denitrosation reaction (Tu and Yang, 1985), which results in the formation of nitrite and monomethylamine. There was strong prior laboratory support for this proposed microbial pathway, as the degradation pathway for NDMA by undefined soil consortia has been reported to be accompanied by the appearance of formaldehyde and methylamine (Kaplan and Kaplan, 1985).

To confirm our hypothesized reaction mechanisms, we followed the formation of nitrite and formaldehyde during NDMA biodegradation (Figure 3.4). We observed a relationship between NDMA loss and nitrite formation suggesting a yield of 1 mol of nitrite for every 7 or 8 mol of NDMA degraded. This observation supports the idea that denitrosation is slow compared to the primary hydroxylation pathway, in which nitrogen gas and formaldehyde are produced instead of nitrite and methylamine. This finding is consistent with previous studies of the mammalian NDMA biodegradation pathway. Like nitrite, formaldehyde production corresponds to NDMA disappearance; however, the concentration of formaldehyde rapidly decreases after about 1.5 h, presumably because formaldehyde was degraded by the bacteria. At 1.5 h, the amount of formaldehyde produced accounts for approximately 80% of the NDMA that has disappeared.

### 3.1.5 Environmental Implications and Future Research

The majority of our identified NDMA-degrading bacteria were selected for this study because they were well-characterized laboratory strains that expressed monooxygenase enzymes with a demonstrated relaxed specificity to xenobiotic substrates such as MTBE and TCE. Though they were all originally isolated from the environment and are members of common soil genera such as *Pseudomonas*, *Mendocina*, and *Mycobacteria*, they all required specific inducing conditions, such as copper limitation or the addition of potentially toxic substrates (e.g., propane or toluene) to trigger enzyme activity. In contrast, the *Rhodococcus* strain isolated in our laboratory grows on nontoxic and environmentally common simple energy sources (e.g., digested soy broth) while still possessing the capability to biodegrade NDMA. As a result, this *Rhodococcus* strain is a good model for NDMA biodegradation in soil and groundwater systems. Furthermore, the finding that a propane-induced enzyme in strain RR1 has the capability to enhance its NDMA degradation activity by 40 times has potential for application to hazardous waste site remediation.

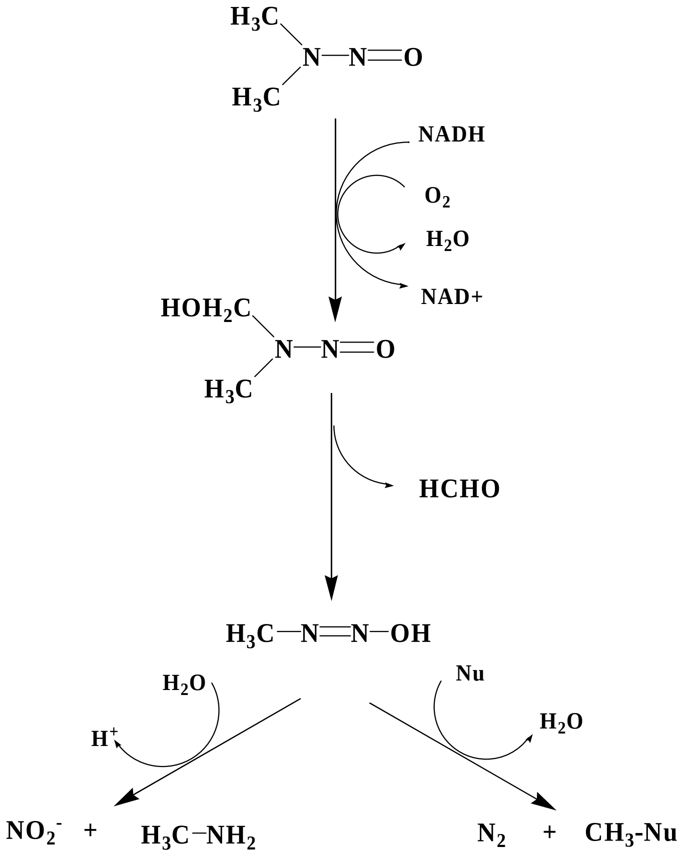


**Figure 3.3. Proposed Pathway for Aerobic NDMA Metabolism.**

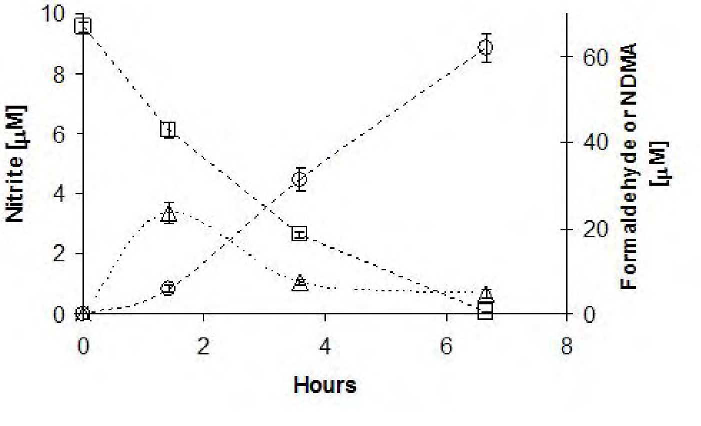


**Figure 3.4. Degradation of NDMA and Production of Formaldehyde and Nitrite by *Rhodococcus sp*. RR1 (~60 Mg of Protein/L) Grown on Propane.**
Key: hollow squares = NDMA loss; hollow triangles = formaldehyde production; hollow circles = nitrite production.

In the future, we hope to characterize the environmental relevance of our identified strains by investigating the influence of relevant co-contaminants on NDMA biodegradation. Specifically, we plan to assess biodegradation in synthetic and actual wastewater matrixes using the organic carbon naturally found in these systems to determine if this substrate promotes or hinders NDMA biodegradation. Furthermore, we also plan to study the use of propane as a biostimulant for NDMA removal in soil matrices.

## 3.2 NDMA BEHAVIOR IN SOILS

Once in soil, the potential for NDMA to move to groundwater will depend on its rate of biotransformation and the extent of its adsorption onto surfaces. Due to its relatively high polarity, retention of NDMA by soils is generally weak (Gunnison et al., 2000; Mitch et al., 2003b). Therefore, sorption is important to NDMA fate and transport mainly because it retards the transport of the compound, thereby giving bacteria additional opportunities to degrade the compound. The research described in section 3.1 suggests that NDMA will undergo biodegradation in the presence of certain strains of bacteria that express monooxygenase enzymes. However, the existence of biodegradation pathways for NDMA does not guarantee the degradation of the compound in situations in which water reuse is practiced, because microbial ecology and transport processes will lead to conditions that are more complex than those encountered in simple laboratory experiments.

Previous research from studies that employed soil microcosms suggests that NDMA degradation can occur under the complex conditions encountered in soil and groundwater. However, results from previous studies are inconsistent with respect to the rates and extent of NDMA degradation. For instance, Mallik and Tesfai (1981) observed limited NDMA degradation by soil microorganisms with losses of only 6–9% after 20 h of incubation at 30 °C. Tate and Alexander (1975, 1976) also reported a long lag time and slow degradation of NDMA in soil at 60 mg/kg and difficulties in isolating NDMA degraders from soil or sewage. However, in a more recent study by Gunnison et al. (2000), NDMA biodegradation was reported with native soil microorganisms cultured under both anaerobic and aerobic conditions. In addition to inconsistencies in the previous data, previously published studies are not particularly relevant to systems in which water reuse is practiced. The research described in this section addresses biodegradation of NDMA in soils under conditions that are more relevant to landscape irrigation and groundwater recharge.

### 3.2.1 Materials and Methods

NDMA standards and stock solutions were prepared from a neat liquid purchased from Sigma-Aldrich (Milwaukee, WI) and were used as received. The deuterium-labeled NDMA ($d_6$-NDMA, 98%) was purchased from Cambridge Isotope Laboratories (Andover, MA) and used as a surrogate in NDMA analysis. Solvents and other chemicals were all gas chromatography (GC) or analytical reagent grade.

The three landscape soils used in the sorption and biotransformation experiments were collected from a field site located at the Agricultural Experiment Station on the campus of University of California in Riverside, CA. The original soil was a Hanford sandy loam containing 0.3% organic matter. In 1995, plots (8 by 8 m) were constructed and then planted with tall fescue grass (*Festuca arundinacea*), a low-growing groundcover spring cinquefoil (*Potentilla tabernaemontani*), or pear trees (*Pyrus calleryana*). At the time of sampling, the plots of turfgrass and groundcover had 100% cover by vegetation, while the plots of pear trees had a single tree at the center of the plot and the soil surface was mostly bare. Soil cores

(10 cm [length] and 5 cm [i.d.]) were randomly taken from plots with the same planting cover using a hand auger. The fresh soil samples were pooled for the same vegetation type, passed through a 2-mm sieve without complete air drying, and stored in plastic bags at room temperature before use. Basic soil chemical and physical properties are given in Table 3.2.

The test soils were further analyzed for their microbial characteristics. Soil microbial biomass was determined as extractable lipid phosphate (lipid-P) by using a modified Bligh and Dyer procedure described by Kates (1986). Soils were also measured for dehydrogenase activity (DHA). Soil DHA is considered a good indicator for soil microbial activity, as dehydrogenases are believed to occur only within the living cells. Soil DHA was determined by using a modified procedure described by Burns (1978). The measured soil biological parameters are shown in Table 3.2.

Batch experiments were conducted to determine NDMA adsorption on the landscape soils. Briefly, 10 g of soil (dry weight equivalent) and 10 mL of 0.01 M $CaCl_2$ aqueous solution were mixed in 40-mL Teflon centrifuge tubes at low speed for 24 h on a mechanical shaker. An aliquot of 25, 50, 100, 250, 500, or 1000 µL of 50-mg/L NDMA aqueous solution was added into the slurry, and the spiked samples were mixed at high speed on the shaker for another 24 h. Phase separation was achieved by centrifuging the sample tubes at 1500 × *g* for 20 min. To determine NDMA concentration in the aqueous phase, a 1.0-mL aliquot of the supernatant was transferred to a 20-mL glass vial containing 5.0 mL of dichloromethane and 5 g of anhydrous sodium sulfate. After addition of 0.1 mL of $d_6$-NDMA (10 mg/L, in dichloromethane), the vial was capped with an aluminum seal and a Teflon-lined butyl rubber septum and was vigorously mixed by hand for 2 min. The dichloromethane phase was then transferred into a GC vial and analyzed on a GC–mass spectrometer system (GC-MS). After the solution was decanted, the remaining soil was mixed with 5 g of anhydrous sodium sulfate, 5.0 mL of dichloromethane, and 0.1 ml of the $d_6$-NDMA solution (10 mg/L, in dichloromethane) at high speed for 4 h on the shaker. The sample tube was centrifuged at 1500 × *g* for 10 min, and an aliquot of the solvent phase was analyzed by GC-MS. Three replicates were used for each concentration level.

**Table 3.2. Selected Properties of the Landscape Soils Used to Study Sorption and Biotransformation of NDMA**

| **Property** | **Value for:** | | |
|---|---|---|---|
| | **Turfgrass** | **Groundcover** | **Bare surface** |
| Organic matter (%) | 0.96 | 1.63 | 0.65 |
| Clay (%) | 10 | 10 | 10 |
| Silt (%) | 26 | 29 | 29 |
| Sand (%) | 64 | 61 | 61 |
| Cation exchange capacity (meg/100 g) | 7.7 | 8.4 | 6.3 |
| pH | 7.4 | 6.4 | 7.8 |
| Microbial biomass (nmol of lipid-P/g of soil) | 64 ± 1[1] | 71 ± 2 | 20 ± 1 |
| DHA (µg of TPF/g of soil) | 134 ± 19 | 160 ± 16 | 43 ± 9 |

[1] Values following the "±" sign are standard deviations of three replicates.

Degradation of NDMA in landscape soils was determined through incubation experiments under controlled conditions. The initial soil water content was 12% (w/w). Fifty grams of soil (dry weight equivalent) was weighed into 125-mL glass serum bottles and spiked with 2.5 mL of NDMA aqueous solution. The spiked bottles were closed by capping with aluminum seals and Teflon-lined butyl rubber septa and mixed thoroughly by shaking with hand. The sample bottles were incubated in the dark, and triplicate samples were removed 0, 3, 7, 14, 21, 28, and 56 days after the treatment. Soil samples were spiked with 0.1 mL of $d_6$-NDMA in dichloromethane (10 mg/L) as a surrogate and extracted with 50 mL of dichloromethane by shaking at high speed for 4 h. The solvent extract was filtered through a funnel containing 20 g of anhydrous sodium sulfate, and the dried extract was concentrated to a final volume of about 1 mL under a stream of dry nitrogen. An aliquot of the final extract was used for analysis by GC-MS. The recovery of NDMA was determined to be 36.6 ± 6.6, 39.0 ± 5.4, and 37.4 ± 7.2% for the tree soil, turfgrass soil, and groundcover soil, respectively. However, as $d_6$-NDMA was used as a surrogate, and the results were not corrected for recovery. The detection limit of NDMA under the above protocol was 0.20 µg/kg.

A number of paired treatments were used to understand the mechanism of NDMA degradation in soil and the effect of treatment and environmental conditions. In the first paired treatments, one set of soil samples was autoclaved to remove biological activity before NDMA addition, while another set was not sterilized. Sterilization was achieved by autoclaving the soil samples twice at 122 ºC and 17.2 psi. In the second paired treatments, the landscape soils were treated at two different concentrations of NDMA to understand the effect of NDMA concentration on its persistence. The higher concentration was 250 µg/kg, while the lower concentration was 25 µg/kg. While these concentrations are higher than the concentrations of NDMA expected in soils where landscape irrigation with recycled water occurs, they are closer to realistic concentrations than those cited in most previous studies. In the third paired treatments, the treated samples were incubated at two different temperatures to understand the effect of temperature on NDMA persistence. The treated samples were incubated at either room temperature (21 ± 1 °C) or at 10 °C in an incubator. In the fourth paired treatments, nonsterilized turfgrass soil was amended with anthropogenic nutrient sources to understand the potential effect of fertilization on NDMA persistence. One set of samples was amended with compost steer manure (0.5 g per container; Earthgro, Marysville, OH), and the other set was treated with calcium nitrate (5 mg per container), 1 day before NDMA treatment.

To analyze NDMA in the final sample extract, a 1.0-µL aliquot was injected into an Agilent 6890N GC (Agilent, Wilmington, DE) equipped with a split/splitless inlet and an Agilent 7683 autosampler. An Agilent 5973 mass-selective detector operating in the electron-impact ionization mode (EI) was used in the selective ion monitoring (SIM) mode with selected ions at 74 (NDMA) and 80 ($d_6$-NDMA) *m/z* for detection. The column was a 30-m (length) × 0.25-mm (i.d.) × 0.25-µm (film thickness) DB-1701 capillary column. The interface temperature was maintained at 280 °C. Ion source and quadrupole temperatures were kept at 230 and 150 °C, respectively. Pulsed splitless injection was used with a pressure of 0.17 MPa for 0.3 min and a splitless time of 0.4 min. Helium was used as the carrier gas with a flow rate of 1.0 mL/min, and the inlet temperature was maintained at 210 °C. The oven temperature was programmed with an initial temperature of 45 °C for 2 min, increased at 50 °C $\min^{-1}$ to 100 °C, held for 2 min, increased at 50 °C $\min^{-1}$ to 280 °C, and finally held for 1.5 min. The retention times of NDMA and $d_6$-NDMA were 4.49 and 4.47 min, respectively. The ratio of response factor between NDMA and $d_6$-NDMA under the conditions cited was 1.21, which was used for quantification of NDMA.

### 3.2.2 NDMA Adsorption in Landscape Soils

Adsorption isotherms of NDMA in three landscape soils were well described by a linear relationship ($r^2 > 0.95$) (Figure 3.5), from which the linear partition coefficient $K_d$ was obtained by using

$$C_s = K_d \times C_w \qquad (1)$$

where $C_s$ is NDMA concentration in the soil phase (micrograms per kilogram) and $C_w$ is NDMA concentration in the aqueous phase (micrograms per liter). The obtained $K_d$ values were further used to derive the organic carbon normalized partition coefficient $K_{OC}$ (Table 3.3). Adsorption in all three soils was weak, with $K_d < 1$ L/kg, and the difference between soils was small. The estimated $K_{OC}$ ranged from 68 to 118, suggesting again that NDMA was

**Table 3.3. Distribution Coefficient $K_d$ and Organic Carbon Normalized Distribution Coefficient $K_{OC}$ of NDMA in Different Landscape Soils**

| | OM (%)[1] | OC (%)[2] | $K_d$ (L/kg) | $r^2$ | $K_{OC}$ (L/kg) |
|---|---|---|---|---|---|
| Turfgrass | 0.96 | 0.56 | 0.56 ± 0.01 | 0.99 | 100 ± 2 |
| Groundcover | 1.63 | 0.94 | 0.64 ± 0.01 | 0.99 | 68 ± 1 |
| Bare surface | 0.65 | 0.38 | 0.45 ± 0.02 | 0.97 | 118 ± 5 |

[1] OM, organic matter content.
[2] OC, organic carbon content.

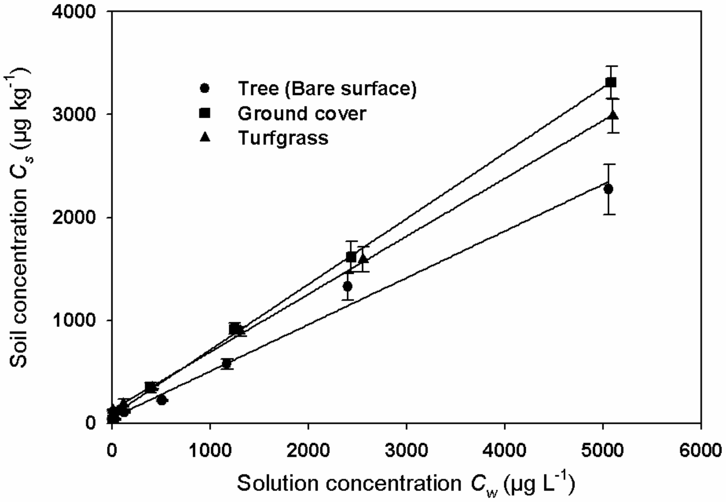


**Figure 3.5. Linearized Adsorption Isotherms of NDMA in Three Different Landscape Soils at 21 °C.**

Vertical bars indicate standard deviations.

weakly adsorbed in the landscaped soils. Similar results were obtained by Gunnison et al. (2000) in their study of subsurface soil samples including sand, sandy loam, and loamy sand soil, with $K_d$ values ranging from 0.4 to 1.2 L/kg. The weak adsorption suggests that, although NDMA is mobile in landscape soils, its transport will be retarded to some degree by sorption to soil. For example, in a soil with 1% organic carbon and 10 kg of soil/L of water, approximately 90% of the NDMA will be associated with soil surfaces at equilibrium. Therefore, sorption is important inasmuch as it allows other attenuation mechanisms, such as biodegradation, to occur as the NDMA-containing water percolates through the soil.

### 3.2.3 NDMA Sorption and Biotransformation in Soils

Results from the incubations of NDMA in the presence of the three landscape soils are shown in Figure 3.6 and Tables 3.4 through 3.6. Under all conditions tested, the NDMA disappeared. The dissipation of NDMA in different landscape soils was fitted to a first-order decay model to facilitate comparison of the different conditions. The fits of the first-order plots were generally good ($r^2 > 0.85$) when NDMA degradation was relatively fast but were poor ($r^2 < 0.60$) when NDMA degradation was slow (e.g., following sterilization treatment).

Sterilization by autoclaving reduced the rate of NDMA disappearance in all soils and at both NDMA treatment levels (Figure 3.6 and Table 3.4). Assuming that the NDMA degradation observed in the sterile control was attributable to abiotic loss pathways and not to bacterial contamination of the autoclaved soil samples, the overall rate constant $k$ can be modeled as the sum of the rate constant for abiotic losses
($k_c$, day$^{-1}$) and biological degradation ($k_b$, day$^{-1}$):

$$k = k_c + k_b \qquad (2)$$

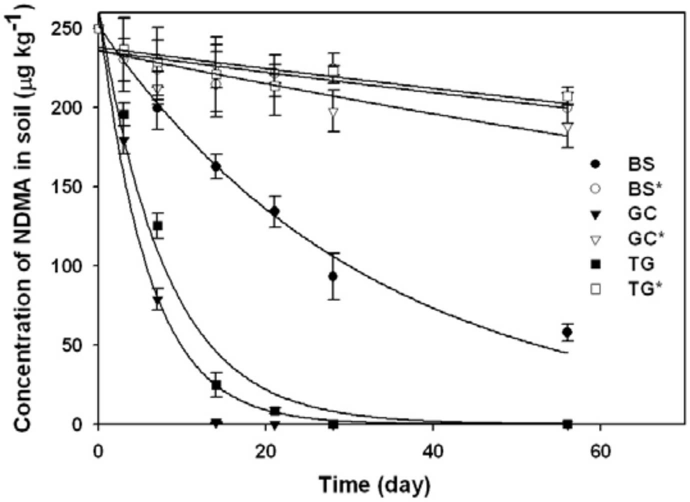


**Figure 3.6. Degradation of NDMA in Different Landscape Soils at 21 °C.** Vertical bars are standard deviations. BS = bare surface soil; BS* = autoclaved bare surface soil; GC = groundcover soil; GC* = autoclaved groundcover soil; TG = turfgrass soil; TG* = autoclaved turfgrass soil.

**Table 3.4. First-Order Rate Constants for NDMA Degradation in Landscape Soils following Different Pretreatments at 250 µg/Kg (21 °C)**

| **Soil** | **k (day$^{-1}$)** | ***T*$_{1/2}$ (day)** | ***r*$^2$** |
|---|---|---|---|
| | | Nonsterilized | |
| Turfgrass | 0.124 ± 0.008 | 5.6 ± 0.4 | 0.98 |
| Groundcover | 0.168 ± 0.011 | 4.1 ± 0.3 | 0.98 |
| Bare surface | 0.031 ± 0.002 | 22.5 ± 1.2 | 0.96 |
| | | Sterilized | |
| Turfgrass | 0.003 ± 0.001 | 217 ± 54 | 0.40 |
| Groundcover | 0.005 ± 0.001 | 151 ± 33 | 0.56 |
| Bare surface | 0.003 ± 0.001 | 231 ± 61 | 0.44 |
| | | Nutrient amendment[1] | |
| Organic matter | 0.136 ± 0.009 | 5.1 ± 0.3 | 0.94 |
| Calcium nitrate | 0.115 ± 0.011 | 6.0 ± 0.6 | 0.90 |

[1] Treatments in turfgrass soil.

**Table 3.5. First-Order Rate Constants and Half-Lives for NDMA Degradation in Landscape Soils at Different NDMA Initial Concentrations (21 °C)**

| **Soil** | **k *(d$^{-1}$)*** | ***T*$_{1/2}$ *(d)*** | ***r*$^2$** |
|---|---|---|---|
| | | 250 µg kg$^{-1}$ | |
| Turfgrass | 0.124 ± 0.008 | 5.6 ± 0.4 | 0.98 |
| Groundcover | 0.168 ± 0.011 | 4.1 ± 0.3 | 0.98 |
| Bare surface | 0.031 ± 0.002 | 22.5 ± 1.2 | 0.96 |
| | | 25 µg kg$^{-1}$ | |
| Turfgrass | 0.136 ± 0.006 | 5.1 ± 0.2 | 0.94 |
| Groundcover | 0.173 ± 0.012 | 4.0 ± 0.3 | 0.97 |
| Bare surface | 0.047 ± 0.003 | 14.8 ± 1.1 | 0.90 |

**Table 3.6. First-Order Rate Constants and Half-Lives for NDMA Degradation in Landscape Soils at Different Temperatures (Initial NDMA Concentration = 250 µg/Kg)**

| **Soil** | ***k* (day$^{-1}$)** | ***T*$_{1/2}$ (day)** | ***r*$^2$** |
|---|---|---|---|
| | | 21 °C | |
| Turfgrass | 0.124 ± 0.008 | 5.6 ± 0.4 | 0.98 |
| Groundcover | 0.168 ± 0.011 | 4.1 ± 0.3 | 0.98 |
| Bare surface | 0.031 ± 0.002 | 22.5 ± 1.2 | 0.96 |
| | | 10 °C | |
| Turfgrass | 0.047 ± 0.003 | 14.6 ± 0.8 | 0.95 |
| Groundcover | 0.082 ± 0.007 | 8.4 ± 0.7 | 0.91 |
| Bare surface | 0.019 ± 0.001 | 36.1 ± 2.4 | 0.87 |

The rate constant $k_b$ was estimated from the difference between the paired nonsterile and sterilized treatments, from which the relative contribution of microbial degradation to the overall NDMA degradation was calculated. In all landscape soils, degradation of NDMA was largely attributable to biological degradation at both NDMA treatment levels. In the bare-surface soil, $k_b$ contributed 85–91% of $k$, while in the groundcover and turfgrass soils, the contribution was >95%. The effect of sterilization is consistent with that found by Mallik and Tesfai (1981), who investigated the loss of NDMA in three different soil types (sandy loam, silt loam, and clay) and found the loss of NDMA was higher in nonautoclaved soils than in autoclaved soils. Oliver et al. (1979) used $^{14}$C-NDMA in an aerobic degradation study and found that nitrosamines were degraded to $CO_2$ in nonsterile soils but not in sterilized soils. Similar results were also found in sewage samples by Tate and Alexander (1975), who reported that the rate of NDMA loss from sewage decreased after autoclaving treatment. Therefore, from this and other studies, it may be concluded that NDMA degradation in soils is attributable mainly to soil microorganisms and that the small losses observed in the sterilized controls are negligible.

The persistence of NDMA also differed significantly among different landscape soils. The overall rate of degradation followed the order groundcover soil > turfgrass soil > bare-surface soil. When the initial NDMA concentration was 250 µg/kg, $T_{1/2}$ was estimated to be 4.1 days for the groundcover soil, 5.6 days for the turfgrass soil, and 22.5 days for the bare surface soil. A very similar trend was observed also for the lower NDMA treatment level (Table 3.5). Linear regression analysis was performed between $k$ values for the different soils and the corresponding soil chemical or biological properties (Table 3.3). A close dependence was identified for soil microbial biomass ($r^2$ = 0.93–0.96) or soil DHA ($r^2$ = 0.92–0.96) for both NDMA treatment levels at 21 °C. Therefore, the different persistence of NDMA in the landscape soils was underlined by the different microbial activity in these soils. Analysis of relationship of $k$ values and soil organic matter also showed a significant linear relationship, with $r^2$ of 0.89. Numerous studies have shown the soil organic matter plays a critical role in soil microbial ecology. Therefore, it is likely that the different planting practices changed soil organic matter quality and quantity in the soil, which in turn changed the makeup and activity of soil microorganisms. The rapid degradation of NDMA in groundcover and turfgrass soils was likely a result of more accumulation of organic matter, which supported an active growth of soil microorganisms contributing to NDMA transformation. In contrast, since the roots were sparse and organic matter accumulation was minimal in the tree soil, the microbial activity was limited, which led to the slow degradation of NDMA. These findings are consistent with previous studies on biodegradation of organic contaminants in soils. For example, Boyle and Shann (1998) found that the plant species difference could influence rhizosphere microorganisms and that planting tends to significantly increase the rate of xenobiotic mineralization because of its effect on rhizosphere microbial ecology. Gan et al. (2003) observed that herbicides 2,4-D and dicamba were degraded much more rapidly in the groundcover and turfgrass soils than in the bare surface tree soil under aerobic conditions. In landscape irrigation systems that use wastewater effluent, the organic carbon and nutrients remaining in the effluent may help to support an active microbial community in the rhizosphere.

The effect of NDMA treatment level, nutrient amendment, and temperature on NDMA persistence was evaluated through paired treatments. Degradation of NDMA at the lower NDMA level (25 µg/kg) remained unchanged in the groundcover soil and turfgrass soil and was slightly enhanced in the bare surface soil, when compared with degradation at the higher NDMA level (250 µg/kg) (Table 3.5). Kaplan and Kaplan (1985) studied the NDMA mineralization kinetics in soil for 98 days at various concentrations and found that the

NDMA mineralization rate increased by fivefold when the initial concentration was decreased by 4 orders of magnitude from 100 mg/kg to 10 µg/kg. Gunnison et al. (2000) observed an effect of NDMA concentrations on NDMA transformation rates in slurries of contaminated subsurface soils; the NDMA mineralization rate increased by a factor of 3 for a 3-order-of-magnitude decrease in NDMA concentrations from 50 mg/L to 50 µg/L. From these studies, it is apparent that the effect of NDMA concentration may be significant only when the concentrations cover a very wide range. The results also suggest that the biodegradation rates in the field (where NDMA concentrations should be considerably lower than those studied here) will be as high as or higher than those observed in our study.

Addition of composted manure had no significant effect on NDMA persistence in the turfgrass soil when compared to the no-amendment treatment (Table 3.4). In a previous study, Kaplan and Kaplan (1985) investigated the effect of supplemental organic matter on NDMA mineralization and did not observe any effect. Therefore, although NDMA degradation appears to be proportional to the indigenous soil organic matter content, addition of an anthropogenic source of organic matter may not stimulate NDMA degradation over a short time. Addition of a nitrate source also had no effect on NDMA degradation in the landscape soils (Table 3.4).

Degradation of NDMA at 10 °C was generally slower than that at room temperature for the same soil (Table 3.6). For instance, when the initial NDMA treatment level was 250 µg/kg, persistence of NDMA in the landscape soils decreased by about 40–60% at 10 °C when compared to persistence at 21 °C. Similar effects were also observed for the lower-level treatments; degradation rate of NDMA in soils decreased by about 40~50% at 10 °C when compared to 21 °C. It also appears that temperature had a greater effect on NDMA persistence in the turfgrass soil than in the other soils. Therefore, it may be expected that NDMA would have a longer persistence in the landscape soils during cooler seasons and that use of treated wastewater for irrigation during the cooler seasons would pose an enhanced NDMA leaching risk.

## 3.3 BIODEGRADATION OF NDMA PRECURSORS

Although the exact identity of the NDMA precursors present in municipal wastewater effluent is unknown, they are known to consist of low-molecular-weight (i.e., < 1000 Da), nitrogen-containing polymers derived from biological processes (Mitch and Sedlak, 2004). Because the NDMA precursors cannot be measured directly, the most practical way to assess their fate is to measure the concentration of NDMA formed after subjecting a water sample to disinfection with chloramines (Mitch et al., 2003). Previous studies of the NDMA precursors with this approach have shown that the precursors are not removed from wastewater during extended biological contact in nitrification/denitrification systems employed by WWTPs (Mitch and Sedlak, 2004). The studies also have shown that the precursors are not simple, easily metabolized biopolymers, such as proteins, carbohydrates, or extracellular polymers. As a result of the stability of the NDMA precursors, it is possible that they will persist in the soil and groundwater systems as well as in surface waters.

To obtain a better understanding of the stability of NDMA precursors in the aquatic environment, a series of experiments was conducted by using NDMA precursors from different WWTPs. The NDMA precursors were incubated in the presence of bacteria isolated WWTPs, and the concentration of NDMA formed upon chloramination was measured. These preliminary studies of the stability of NDMA precursors provide insight that can be used to assess the potential for the precursors to enter water supplies in areas where indirect potable reuse and landscape irrigation with wastewater effluent are employed.

### 3.3.1 Materials and Methods

All chemicals used in the studies of NDMA precursor fate were analytical grade and were purchased from Fisher Scientific or Sigma-Aldrich. Glassware used to prepare reagents and to conduct experiments was washed with water treated with a Barnstead Nanopure II system, rinsed with methanol, and baked for 4 h at 450 $^{o}$C. Nanopure water was used in all solutions and reagents before March 2004. In all the experiments conducted after March 2004, environmental-grade water from Fisher Scientific was used for preparation of the reagents and for washing of the solid-phase extraction resins due to concerns about contamination of Nanopure water with NDMA and NDMA precursors. Analysis of blanks from each experiment confirmed the absence of contamination with NDMA from the water or other sources. The trace NDMA contamination impeded our ability to assess the fate of the low levels of NDMA originally present in the wastewater effluent samples collected prior to March 2004 but had little effect on the measurements of NDMA precursors because their concentrations were much higher than the contamination and their effect was accounted for by subtraction of blanks.

Grab wastewater effluent samples were collected prior to disinfection from four municipal WWTPs in 12-L Teflon-lined polypropylene containers. The samples were stored on ice in a cooler immediately after collection and were shipped to UC Berkeley by overnight mail. Information on the four WWTPs is included in Table 3.7.

To assess the fate of NDMA precursors in surface waters, five grab samples also were collected from the Santa Ana River, located in Orange and Riverside counties in Southern California, on June 8, 2003. The surface water samples were collected in 12-L fluorinated polypropylene containers (Nalgene) and were kept in coolers packed with ice. The samples were collected prior to the discharge of the Riverside Regional (RR) WWTP into the Santa Ana River at Rubidoux and at four locations downstream of the wastewater effluent discharge point.

Upon arrival in the laboratory, the wastewater effluent samples were passed through 0.2-µm cartridge filters (Polycap 75AS; Whatman) and were chloraminated or chlorinated with initial concentrations of 10 mg of $Cl_2$/L (0.143 mM). The chloramination of the effluent sample collected from TMWRF on 12/02/03 was performed by addition of the $NH_4Cl$ solution to the sample first, followed by addition of the chlorine solution as opposed to the addition of preformed chloramine. After 1 h of simulated chlorine disinfection, the samples were dechlorinated by adding 3.5-mL aliquots of a 31.2 mM sodium sulfite solution until chlorine could not be detected in the sample by using the DPD total chlorine method (APHA, 1998). Unchlorinated control treatments also were included in the experiments.

The stock chlorine solutions were prepared daily at a concentration of 14 or 20 mM. Free chlorine was prepared by diluting Fisher brand 5% NaOCl solution with Nanopure water or environmental-grade water. The monochloramine solution was prepared by adding concentrated NaOCl dropwise to a 22 mM solution of ammonium chloride in a 1.2:1 ratio of ammonium to chlorine (Kumar et al., 1986). The pH was adjusted to 8.0 prior to the addition of chlorine to minimize the formation of dichloramine and trichloroamine. The total concentration of chlorine in each of the stock solutions was standardized in triplicate by using iodometric titration (American Public Health Association, 1998).

### Table 3.7. WWTPs Where NDMA Precursors Were Collected

| Wastewater treatment plant | Location | Date(s) sampled | Design capacity | Treatment processes |
|---|---|---|---|---|
| Truckee Meadows Water Reclamation Facility (TMWRF) | Reno, NV | Sept 18, 2003<br>Dec 2, 2003<br>March 18, 2004 | 1.24 $m^3/s$ (28 mgd) | Activated sludge, nitrification/denitrification, chlorination/dechlorination |
| Mt. View Sanitary District WWTP (Mt. View WWTP) | Martinez, CA | Dec 30, 2003 | 0.1 $m^3/s$ (1.8 mgd) | Trickling filter, nitrification, UV disinfection, treatment of wetlands |
| Whittier Narrows WRP (WN WWTP) | El Monte, CA | Dec 30, 2003 | 0.7 $m^3/s$ (15 mgd) | Combined nitrification and secondary treatment, sand filtration, chlorination, dechlorination |
| RR WRP (RR WWTP) | Riverside, CA | May 25, 2004 | 1.4 $m^3/s$ (33 mgd) | Activated sludge, partial nitrification/denitrification, chlorination, dechlorination |

After dechlorination, the wastewater effluent samples were inoculated with approximately 2.5 mL of activated sludge mixed liquor/L collected freshly from the WWTP where the wastewater sample was obtained, except for Mountain View WWTP and WN WWTP effluent samples collected on December 30, 2003. Due to the absence of suspended solids (SS) in the trickling filter system at the Mountain View WWTP, the effluent samples of the Mountain View WWTP and WN WWTPs were inoculated with a mixture consisting of equal volumes of freshly collected activated sludge and nitrification tank mixed liquors from the WN WWTP and the primary settling sludge from the Mountain View WWTP. The bacterial inocula total SS concentration ranged between 1120 and 2260 mg/L, with a median of 1610 mg of SS/L.

After inoculation with the activated sludge cultures, the samples were placed in 4-L glass containers and were covered with nonwoven fabric pads to allow gas transfer and to avoid the introduction of foreign particles into the samples. The samples were maintained at room temperature and were mixed by gently shaking twice daily. To distinguish the effects of bacteria from physical processes such as adsorption to the walls of the container, sterilized controls prepared by amending the samples with $HgCl_2$ were used. The viability of the cells in the sterilized treatments was checked by streaking samples on plates with bacterial growth media at the beginning and end of the experiments. No growth was observed in any of the sterilized controls.

The NDMA precursors were converted into NDMA by using the method developed by Mitch et al. (2003a). NDMA concentrations before and after chloramination were analyzed by using a slightly modified version of a previously published solid-phase extraction method, where the solid phase was extracted twice with 1 mL of methylene chloride and blown down to 1 mL (Choi and Valentine, 2002; Choi and Valentine, 2003). Due to the contamination of the Nanopure water system with NDMA, the background NDMA concentration in the experiments conducted in January 2004 was approximately 20 ng/L.

### 3.3.2 Biodegradation of NDMA Precursors

The initial NDMA precursor concentration in the wastewater effluent samples ranged from 190 to 1200 ng/L (Table 3.8 and Figure 3.7). The concentration of NDMA precursors did not change upon exposure to chloramines, but when the samples were exposed to free chlorine, the NDMA precursor concentrations decreased by approximately 70%. The only exception was the sample collected from TMWRF on December 2, 2003, in which the concentration of the NDMA precursors decreased by approximately 60 and 90% when exposed to chloramines and free chlorine, respectively.

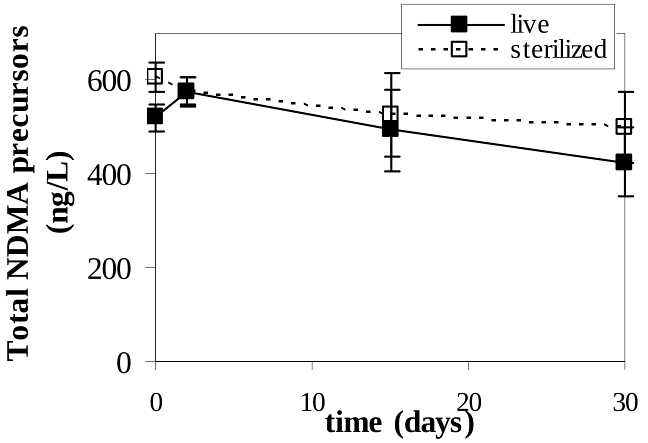
NDMA precursors in untreated effluent samples and in chloraminated effluent samples were very stable with less than 30% loss over 20 to 30 days in most of the incubations. The sample collected from the TMWRF facility on December 2, 2003, behaved differently from the other samples, with a decrease in the concentration of NDMA precursors in the unchlorinated sample of approximately 80% over 30 days. As a result, the concentration of the NDMA precursors in the unchlorinated sample was similar to that observed in the chloraminated sample at the end of the 30-day incubation. The differences between the NDMA precursor concentrations in the live treatments and the sterile controls for unchlorinated and chloraminated wastewater effluent collected from the WN WWTP were not statistically significant ($P > 0.05$).

**Table 3.8. Concentrations of NDMA Precursors during Incubation Experiments**

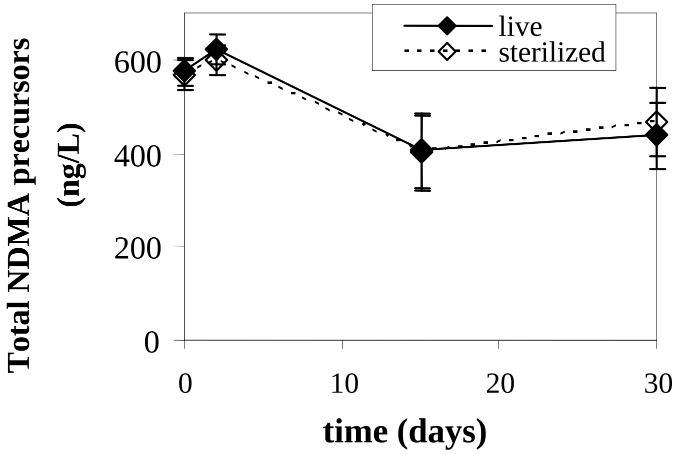
| WWTP, sampling date | Sample ID | NDMA precursor concn (ng/L) (mean ± SD) at: | | | |
|---|---|---|---|---|---|
| | | *t* = 0 days | *t* = 2 days | *t* = 20 days | *t* = 30 days |
| TMWRF, Sept 18, 2003 | Nonchlorinated | 188 ± 6 | 191 ± 4 | 196 ± 7 | |
| | Chlorinated | 49 ± 5 | 34 ± 4 | 43 ± 1 | |
| TMWRF, Dec 2, 2003 | Nonchlorinated | 1220 ± 45 | 845 ± 94 | 453 ± 6 | 195 ± 35 |
| | Chlorinated | 151 ± 61 | 139 ± 7 | 32 ± 5 | 656 ± 20 |
| | Chloraminated | 466 ± 86 | 441 ± 140 | 144 ± 114 | 273 ± 13 |
| TMWRF, March 18, 2003 | Nonchlorinated | 535 ± 60 | 488 ± 20 | 453 ± 39 | 427 ± 17 |
| | Chlorinated | 81 ± 6 | 43 ± 1 | 147 ± 10 | 161 ± 3 |
| | Chloraminated | 538 ± 10 | 489 ± 56 | 494 ± 51 | 445 ± 19 |
| WN, Dec 30, 2003 | Nonchlorinated | | 578 ± 70 | 404 ± 33 | 391 ± 46 |
| | Chlorinated | 184 ± 50 | 139 ± 67 | 32 ± 33 | 656 ± 25 |
| | Chloraminated | 558 ± 59 | 467 ± 68 | 380 ± 33 | 301 ± 83 |
| Mt. View, Dec 30, 2003 | Nonchlorinated | 568 ± 59 | 499 ± 47 | 404 ± 18 | 392 ± 18 |
| | Chloraminated | 502 ± 57 | 464 ± 21 | 471 ± 34 | 370 ± 49 |
| RR, May 25, 2004 | Nonchlorinated | 520 ± 30 | 577 ± 31 | 494 ± 87 | 426 ± 72 |
| | Nonchlorinated/sterile | 606 ± 31 | 577 ± 31 | 525 ± 90 | 426 ± 74 |
| | Chlorinated | 103 ± 7 | 76 ± 8 | 141 ± 13 | 144 ± 18 |
| | Chlorinated/sterile | 105 ± 14 | 105 ± 9 | 88 ± 12 | 110 ± 15 |
| | Chloraminated | 575 ± 31 | 623 ± 31 | 405 ± 80 | 438 ± 72 |
| | Chloraminated/sterile | 568 ± 30 | 600 ± 31 | 402 ± 80 | 467 ± 73 |

For the samples that were subject to free chlorine, the effect of bacteria on NDMA precursor concentrations was not as clear as for the chloraminated and untreated samples. The NDMA precursor concentration did not change during the incubation in two samples (TMWRF collected on September 18, 2003, and WN WWTP) but almost doubled in one sample (TMWRF collected on March 18, 2003) and increased by more than three times in the TMWRF effluent collected on December 2, 2003. The effect of free chlorine on NDMA precursor concentrations was complicated because $HOCl/OCl^-$ could convert the NDMA precursors into species that did not yield NDMA when they were exposed to high concentrations of chloramines during the NDMA precursor test. For example, free chlorine reacts with secondary amines to form chlorinated amines (reviews by Kovacic et al., 1970; Jolley and Carpenter, 1981; Armesto et al., 1998). The chlorinated amines react with chloramines to form NDMA at much lower rates than in their unchlorinated analogs (Mitch and Sedlak, 2002). A similar finding was also reported by Wilczak et al. (2003), who observed that exposure of surface water to 4 mg of HOCl/L for 3 h prior to the chloramination decreased the NDMA formed upon chloramination by approximately an order of magnitude (Wilczak et al., 2003).

a) Unchlorinated treatment



b) Chloraminated treatment



c) Chlorinated treatment

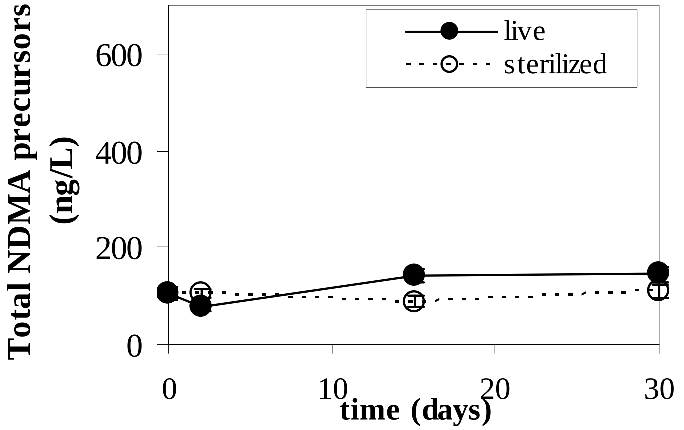


**Figure 3.7. Concentrations of NDMA Precursors during Incubation Experiments Conducted with Effluent from the RR WWTP.**

The increase in NDMA precursor concentrations during the incubation of the free-chlorine-treated samples implies that the reaction that decreased the NDMA precursor concentration was reversible. Although previously believed to happen instantaneously, chlorine-substituted organic amines are not converted to their original forms by bisulfite under the conditions employed in wastewater disinfection systems (Jensen and Helz, 1998) and in our experiments. Therefore, it is possible that the Cl-substituted amines slowly decomposed back to their original forms during the 30-day incubation.

The wastewater effluent used in these experiments contained between 15 and 130 ng of NDMA/L prior to start of the incubations. Hence, when the incubation experiments were conducted, data also were obtained on the removal of NDMA by bacteria. In all of the experiments, the NDMA concentration decreased by more than 50% over the 30-day incubation period. In several cases the concentration of NDMA decreased below the limit of detection of the GC-MS-MS method used in the study (i.e., 10 ng/L). It was difficult to obtain more precise data because the concentrations often were just above the detection limit, and in several cases, background contamination of the samples with NDMA enhanced the uncertainties in the measurements. No decrease in NDMA concentration was observed in the sterile controls conducted with the wastewater effluent sample collected from the WN WWTP. These results are consistent with results reported for the soil slurry experiments in section 3.2 and provide further evidence that NDMA undergoes biotransformation over a period of 1 to 3 weeks under the conditions encountered in soil and wastewater effluent.

The nitrogen dynamics during the bacterial incubation depended on the source of the wastewater effluent and on the relative concentrations of the different nitrogen species at the beginning of the incubation period. Measurements of the nitrogen dynamics provided insight into the biological processes that occurred during the incubation process.

Due to the relatively high initial $NO_3^-$ concentration in the wastewater effluent samples from the Mountain View and WN WWTPs, it is difficult to detect small changes in DON + $NH_3$ or $NO_3^-$ concentrations that may have occurred during incubation. The concentrations of nitrogen species did not change significantly during the bacterial incubation in the unchlorinated wastewater effluent from the Mountain View and WN WWTPs, as well as the chloraminated wastewater effluent of the Mountain View WWTP ($P > 0.05$ for comparison of initial and final concentrations). In the chloraminated treatment, there was a decrease in DON + $NH_3$ concentration accompanied by an equivalent increase in the nitrate concentration, as would be expected for the decay of chloramines and nitrification of ammonia liberated.

In all three unchlorinated wastewater effluent samples collected from the TMWRF (September 18, 2003; December 2, 2003; and March 19, 2004), the DON + $NH_3$ concentration was approximately 1 mg of N/L at the beginning of the incubation period. The concentration decreased by approximately 40% during the 30-day incubation. The decrease in DON + $NH_3$ concentration was accompanied by an increase in nitrate concentration of approximately 0.4 mg of N/L. This observation is consistent with previous research in nitrogen dynamics at this location (Pehlivanoglu and Sedlak, 2004) and indicates that some of the dissolved organic nitrogen was bioavailable.

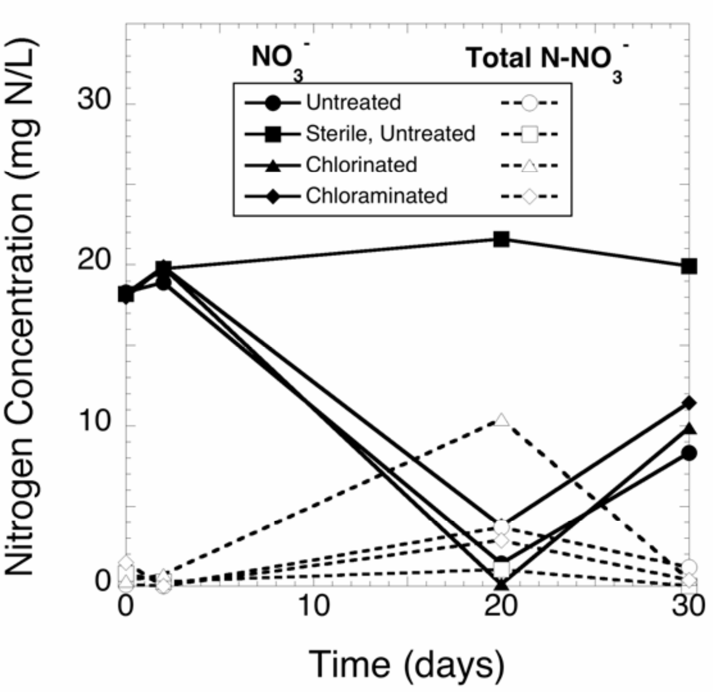


**Figure 3.8. Concentrations of Nitrogen Species during Bacterial Incubation in Samples Collected from the RR WWTP.**

Nitrogen dynamics during bacterial incubation in the RR WWTP effluent sample exhibited behavior different from that observed at the other WWTPs (Figure 3.8). During the 30-day incubation, the concentration of nitrate decreased in all of the live treatments during the first 20 days of the incubation. This decrease was accompanied by an increase in the concentration of other nitrogen species (i.e., organic nitrogen and $NH_3$). The increase in the DON + $NH_3$ concentration accounted for approximately 2 to 8 mg of N/L of the 15 to 18 mg of N (of nitrate) lost. The remainder of the nitrogen may have been incorporated into bacteria. The lack of any changes in the concentration of nitrate or DON + $NH_3$ indicated that there was no bacterial activity in the sterilized treatment.

In five of the six wastewater effluent samples, the concentration of NDMA precursors decreased by less than 50% during the 30-day incubation, with an average decrease of 23% over the course of the experiment. The decrease in the precursor concentration in the sterilized controls was not statistically different from findings for the live treatments ($P = 0.6$ and 0.8 for unchlorinated and chloraminated samples, respectively), suggesting that the small losses observed were not due to biotransformation.

Preliminary experiments with filtering the bacterial inocula immediately before the NDMA precursor test indicated no difference in the NDMA precursor concentrations between the filtered and unfiltered samples, suggesting that the sorption of NDMA precursors onto the biomass cannot explain the modest decrease in the measured concentrations of NDMA precursors, provided that sorption is fast. Previous studies of surface waters also indicated no difference in NDMA precursor concentration between filtered and unfiltered samples (Gerecke and Sedlak, 2003). However, the presence of particle-associated NDMA precursors in unfiltered wastewater effluent samples (Mitch and Sedlak, 2004) suggests that it is possible that NDMA precursors could be lost by adsorption onto the walls of the glass containers used for the incubation in addition to abiotic oxidation.

It is likely that the NDMA precursors in the five wastewater effluent samples in which significant removal was not observed consisted of a suite of different organic nitrogen-containing compounds (Mitch and Sedlak, 2004). The persistence of the NDMA precursors is consistent with the fact that the wastewater effluent had already been exposed to activated sludge or trickling filter bacteria before the incubations and that the easily degraded organic nitrogen-containing compounds (e.g., DMA, amino acids, and polypeptides) had already been removed, leaving behind the more recalcitrant compounds. The low-molecular-weight fraction of DON, which contains DMA and free amino acids and polypeptides, is readily bioavailable, whereas the compounds that do not pass through a 1-kDa ultrafilter are relatively unreactive (Pehlivanoglu and Sedlak, 2004).

The batch biodegradation studies using wastewater inocula indicated that the wastewater-derived NDMA precursors were relatively stable in the presence of bacteria collected from WWTPs, with losses of less than 30% over periods of up to 30 days. In surface waters, effluent-dominated river reaches usually have hydraulic residence times of less than 3 days. Thus, dilution is the only process that will reduce the concentrations of NDMA precursors in effluent-dominated surface waters. It is more challenging to draw conclusions about the fate of NDMA precursors in soil aquifer treatment systems or aquifers based on these data because of the differences in the experimental conditions (e.g., attached vs suspended bacteria, aerobic vs anaerobic conditions). Additional research is needed to simulate an environment where the wastewater is injected into a soil aquifer treatment by using attached bacteria instead of suspended systems or by conducting column studies. Such studies would need to differentiate between biotransformation and sorption because adsorption is more likely to be important in the subsurface.

### 3.3.3 NDMA Precursors in Surface Waters

In the Santa Ana River, the discharge of wastewater effluent from the RR WWTP had little effect on the concentrations of NDMA and had a modest impact on the concentrations of NDMA precursors. Upstream of the RR WWTP discharge, the NDMA concentration was below the detection limit (i.e., 10 ng/L), and the concentration of NDMA precursors was approximately 40 ng/L (Figure 3.9). The concentrations of NDMA and NDMA precursors in the effluent sample from the RR WWTP were 24 and 100 ng/L, respectively (i.e., sample 2 in Figure 3.9). Downstream of the RR WWTP's discharge point, the NDMA concentrations decreased to below the detection limit, whereas the NDMA precursor concentrations remained elevated relative to the concentrations detected in the upstream samples.

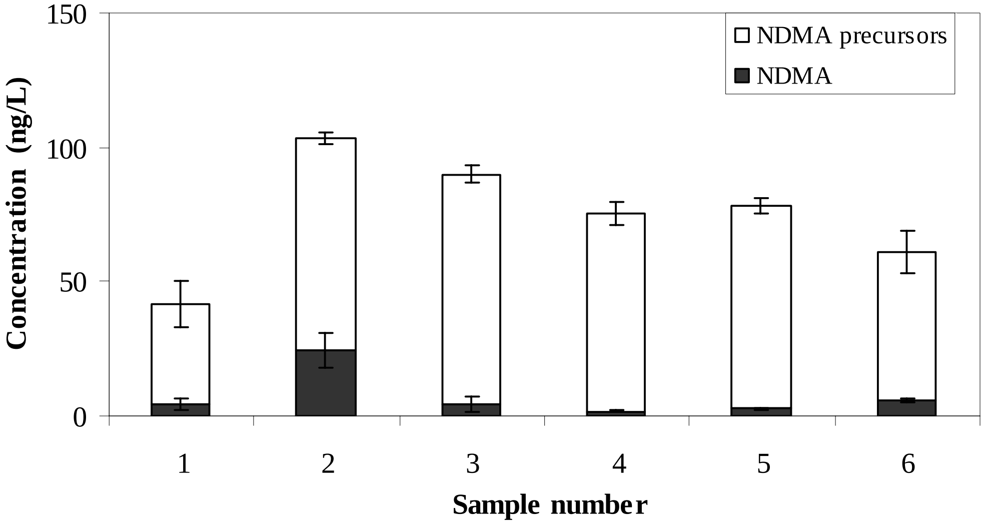


**Figure 3.9. Concentrations of NDMA and NDMA Precursors in Samples Collected from the Santa Ana River.**
Sample 1 was collected above the RR WWTP at Rubidoux; sample 2 was an effluent sample from the RR WWTP; samples 3 through 6 were collected below the RR WWTP at distances spaced by approximately 5 km.

Samples also were collected from an agricultural region of California's Central Valley that is home to numerous dairy operations (Figure 3.10, samples 1B1 to 1B6). The three surface water samples, which consisted of two drainage canals and one small river, contained concentrations of NDMA precursors comparable to those detected in wastewater effluent (e.g., the median concentration of NDMA precursors in the effluent of a series of WWTPs was 1340 ng/L; Sedlak et al., 2005). Two groundwater samples (1B3 and 1B5) collected from the same area also contained relatively high concentrations of NDMA precursors. These two samples were collected from tile drains under farms where dairy waste (cow manure and milking stall wash water) is infiltrated to groundwater. We also collected four additional samples of groundwater from shallow wells in four separate locations on a dairy farm (samples 1C1 to 1C4). NDMA precursor concentrations in these samples were comparable to those detected in the tile drains.

The relatively high concentrations of NDMA precursors detected near dairies in the Central Valley site have interesting implications for water quality in regions where agricultural discharges are important. First, the data indicate that agricultural operations such as dairy farming could act as sources of NDMA precursors. This finding is noteworthy because previous studies indicated that NDMA precursor concentrations in surface and groundwater that were not subject to wastewater discharges were less than 75 ng/L (Gerecke and Sedlak, 2003). In addition, these data suggest that NDMA precursors in animal wastes, which presumably are similar to those in municipal wastewater, can persist in groundwater.

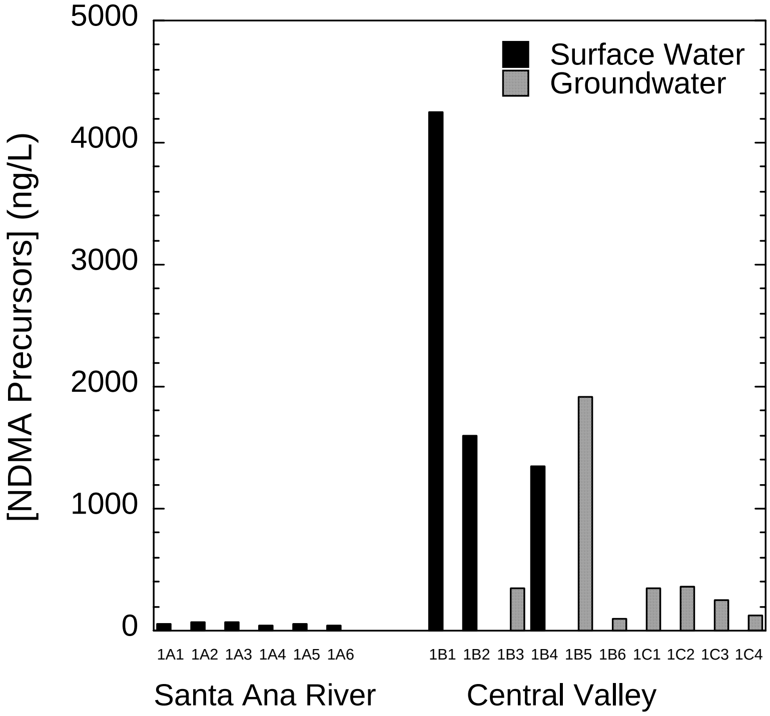


**Figure 3.10. Concentrations of NDMA Precursors Detected in Surface and Groundwater Samples.**

# CHAPTER 4

# FATE OF NDMA AND NDMA PRECURSORS DURING LANDSCAPE IRRIGATION

## 4.1 BACKGROUND

Results from the laboratory studies described in Chapter 3 and previously published data provide a basis for predicting the fate of NDMA and NDMA precursors at sites where wastewater effluent is used for landscape irrigation. The data on NDMA sorption and biotransformation described in sections 3.1 and 3.2 suggest that sorption coupled with biodegradation might result in removal of NDMA as it leaches through the vadose zone, while the data presented in section 3.2 and results from previously published studies indicate that NDMA precursors might persist long enough to leach through the vadose zone. These predictions are based upon laboratory studies conducted at relatively high concentrations and do not adequately simulate the many processes that can affect the fate and transport of contaminants in landscape irrigation systems.

To assess the fate of NDMA and NDMA precursors under the more complicated conditions encountered during landscape application, a field study was carried out during the summer months of 2004 in Riverside, California. Wastewater effluent from the RR WWTP was applied by spray irrigation to turfgrass plots at irrigation rates slightly higher than those typically used for golf courses and similar locations where turfgrass is maintained. Samples collected from lysimeters installed below the vadose zone were analyzed for NDMA and NDMA precursors over a period of approximately 4 months. The measurements from the field study were complemented with additional studies on the fate of NDMA in soil from the field site.

## 4.2 MATERIALS AND METHODS

The field study was carried out in turfgrass plots located near the campus of UC Riverside. The plots were constructed in 1992 and transplanted in 1993. Each plot is 3.66 by 3.66 m and has a separate sprinkler system with four sprinklers situated at each corner. At the time of construction, the top 89 cm was filled with soil, either a loamy sand or a sandy loam, while the bottom layer (7.6 cm) was paved with gravel. At the center of each plot, there is a cluster of five 55-gallon drums filled with the soil and gravel from the site. Leachate from each drum flows through a conduit pipe under gravity and drains to an outlet located at the edge of the field (at a lower elevation). Eight plots were used for this study. The irrigation systems for these plots were modified before the study to allow for the use of wastewater effluent in the irrigation system.

Tertiary treated wastewater effluent, collected after chlorination, was transported with a water truck from the City of Riverside WWTP in Riverside, California (see Table 3.7 for details of the plant size and configuration) and stored in a large (6000-gal) green polyethylene tank next to the plots. Prior to the study, wastewater effluent was stored in the tank for 28 days, during which NDMA and NDMA precursor concentrations were monitored. NDMA and NDMA precursors were stable in the water under the storage conditions, and no significant decrease in NDMA concentration was observed. A total of five tanks of treated wastewater were consumed for the 113-day field study. Once each week, triplicate samples were taken from the tank and analyzed for NDMA concentrations.

The irrigation rate was 110–130% of the potential evapotranspiration rate (i.e., ETo) from June 14 to September 2, 2004, and was increased to 160% of ETo after September 3 to raise the leaching rate. The ETo was measured on a daily basis at the field site, and the ETo from the previous week was used to modify the actual irrigation rate for the subsequent week. The irrigation rates were higher than those that are normally used for turfgrass. The higher rates of irrigation were used to generate adequate volume of leachate and to create conditions with the highest potential for leaching of NDMA and NDMA precursors.

Four treatments were included. There were two soil types, a sandy loam soil and a loamy sand. There also were two different irrigation schedules, irrigation at night (from 10:30 p.m.) and irrigation during the day (from 7:30 a.m.). Two replicated plots were included in each treatment. Leachate from each plot was collected in an opaque plastic container with a small opening. Three times a week (on Monday, Wednesday, and Friday), aliquots of leachate samples were transferred into multiple 1-L brown glass bottles and stored at 4 °C if not immediately analyzed. Most samples were analyzed on the same day of sample collection. Approximately half of the samples were sent to UC Berkeley for analysis of NDMA and NDMA precursors. In addition, splits of approximately 10% of the samples were sent to the City of Long Beach’s analytical laboratory for analysis of NDMA. The City of Long Beach has experience analyzing trace concentrations of NDMA in wastewater effluent and participated in a recent WateReuse Foundation project on NDMA analysis. The storage tank was sampled on a weekly basis to determine the concentration of NDMA in the irrigation water.

The method used for analyzing NDMA at UC Riverside is briefly described below. A 1000-mL water sample was spiked with 100 µL of a $d_6$-NDMA stock solution (10 mg of $d_6$-NDMA/L in methylene chloride) in a 2-L glass separatory funnel and then manually mixed with 100 ml of methylene chloride for 2 min. After the methylene chloride phase was collected, the remaining aqueous phase was extracted two additional times with fresh solvent. The extracts were combined, dehydrated with 50 g of anhydrous sodium sulfate, and then concentrated to 0.1–0.2 mL. An aliquot of sample was injected into GC-MS for quantification of the NDMA. Analysis of NDMA was carried out on an Agilent 6890N GC equipped with an Agilent 5973 MSD operating in electron-impact ionization mode. Separation was achieved on a DB-1701 capillary column (30 m [length] × 0.25 mm [i.d.] × 0.25 µm [film thickness]) with a flow rate of 1.0 mL/min (helium). To prevent sample decomposition in the inlet, pulsed splitless injection was used with pressure at 25 psi for 0.5 min, and the total splitless time was 0.51 min. The oven temperature was initially set at 45 °C (2.5 min), ramped to 100 °C at 50 °C/min, held for 2 min at 100 °C, then ramped to 280 °C at 50 °C/min, and finally held at 280 °C for 1 min. Ion source and quadrupole were kept at 230 °C and 150 °C, respectively. The inlet temperature was 210 °C, and the transfer line between GC and MSD was maintained at 270 °C. The mass spectra were obtained by using selected ion monitoring (SIM) at 70 eV. The characteristic ions used for SIM were 74 and 42 for NDMA and 80 and 46 for $d_6$-NDMA. Under the above conditions, the retention time was 4.76 min for $d_6$-NDMA and 4.79 min for NDMA.

Samples were analyzed for NDMA precursors at UC Berkeley by subjecting samples to chloramination as described by Mitch et al. (2003a), using 500-mL samples instead of 1-L samples due to sample volume limitations. Twenty millimolar solutions of monochloramine were prepared by adding sodium hypochlorite to a solution of ammonium chloride at pH 8.0.

To avoid breakpoint chlorination, ammonia was added at slight excess (1:1.2 $OCl^-$ to $NH_4^+$ molar ratio), and the hypochlorite was added slowly to a rapidly mixed solution. Monochloramine solutions were standardized iodometrically. Fifty milliliters of the monochloramine solution was added to each 450-mL sample buffered at pH 6.8, for a final monochloramine concentration of 2.0 mM (140 mg/L as $Cl_2$). The conversion of NDMA precursors to NDMA occurred over a 10-day period, after which the reaction was quenched by addition of excess ascorbic acid. The concentration of NDMA precursors was equal to the amount of NDMA formed during the chloramination reaction.

NDMA concentrations before and after the precursor test were analyzed by using a slightly modified version of a previously published solid-phase extraction method (Taguchi et al., 1994). Five-hundred-milliliter samples were spiked with 25 ng of $d_6$-NDMA per L of methanol; $d_6$-NDMA was used as an internal standard for the GC-MS-MS isotope dilution method (Mitch et al., 2003a). Two hundred milligrams of Ambersorb 572 (Supelco) resin was added to each sample, and the samples were stirred overnight by using a magnetic stir bar or a shaker table. The resin was filtered by using glass-fiber filter paper and allowed to dry overnight. Then the solid phase was extracted with 2 mL of methylene chloride and blown down to a final volume of 500 μL. Analysis of NDMA was performed on a Varian CP-3900 gas chromatograph coupled to a Saturn 2100T mass spectrometer. Splitless injections of 2 μL were separated by using an HP-5MS capillary column (30 m × 0.25 mm [i.d.] × 1 μm; Agilent Technologies). Tandem mass spectrometry was carried out by using methanol as the chemical ionization gas. NDMA was quantified by using the 74.1 *m/z* parent ion and the 44, 47, and 58 *m/z* daughter ions. $d_6$-NDMA was quantified by using the 81.1 *m/z* parent ion and the 50 and 64 *m/z* daughter ions.

## 4.3 RESULTS

### 4.3.1 NDMA and NDMA Precursors in Wastewater Effluent

The concentrations of NDMA in the City of Riverside’s wastewater effluent varied between batches (Table 4.1), with average concentrations ranging from approximately 300 to 1400 ng/L in the five tanks used during the study. Under the experimental conditions, NDMA appeared to be stable during storage in the tank, with little variation in concentrations during the 3 to 4 weeks that the effluent was held in the tank.

The concentration of NDMA precursors in the wastewater effluent applied to the test plots ranged from <5 ng/L to 336 ng/L, with concentrations of NDMA precursors below the limit of quantification (i.e., the reporting limit) in the majority of the samples (Table 4.2). The relatively low concentration of NDMA precursors was unexpected, given preliminary measurements of NDMA precursors that indicated concentrations between 400 and 600 ng of NDMA/L. Furthermore, results from previous studies (Mitch and Sedlak, 2004; Sedlak et al., 2005) indicate that NDMA precursor concentrations in municipal wastewater effluent typically range between 500 and 2000 ng/L. We suspect that the lower-than-expected concentration of NDMA precursors was due to prechlorination of the wastewater effluent with a relatively high dose of free chlorine, which is known to reduce the concentration of NDMA precursors (see section 3.3 for details).

### Table 4.1. NDMA Concentrations in the Wastewater Effluent Used for Irrigation

| Sampling date | Comment | [NDMA] (ng/L) | SD |
|---|---|---|---|
| Jun 14, 2004 | Tank filled | 1170 | 65 |
| Jun 15, 2004 | | 1270 | 303 |
| Jun 16, 2004 | | 1240 | 108 |
| Jun 23, 2004 | | 1480 | 221 |
| Jun 30, 2004 | | 1520 | 166 |
| July 7, 2004 | | 1820 | 420 |
| July 14, 2004 | | 1470 | 252 |
| July 14, 2004 | Tank filled | 400 | 76 |
| July 21, 2004 | | 380 | 59 |
| July 28, 2004 | | 140 | 11 |
| Aug 6, 2004[1] | Tap spiked | 860 | 196 |
| Aug 9, 2004 | Tank filled | 1140 | 186 |
| Aug 11, 2004 | | 960 | 239 |
| Aug 18, 2004 | | 1260 | 393 |
| Aug 25, 2004 | | 1500 | 303 |
| Sept 2, 2004 | | 1220 | 170 |
| Sept 2, 2004 | Tank filled | 591 | 211 |
| Sept 9, 2004 | | 617 | 167 |
| Sept 15, 2004 | | 616 | 252 |
| Sept 17, 2004 | Tank filled | 340 | 34 |
| Sept 22, 2004 | | 203 | 13 |
| Oct 1, 2004 | | 387 | 120 |

[1] On August 6, 2004, approximately 4000 L of tap water spiked with 800 ng of NDMA/L was added to the tanks because the scheduled shipment did not arrive on time. The spiked water was used for two irrigation cycles.

## Table 4.2. NDMA Precursor Concentrations in the Wastewater Effluent Used for Irrigation

| Sampling date | [Precursors] (ng/L) | SD (ng/L) | Comments |
|---|---|---|---|
| Jun 18, 2004 | <50 | NA[1] | Tank filled |
| Jun 21, 2004 | <223 | NA | |
| Jun 21, 2004 | <211 | NA | |
| July 5, 2004 | 336 | 89 | |
| July 9, 2004 | <82 | NA | |
| July 12, 2004 | < 95 | NA | |
| July 16, 2004 | <159 | NA | Tank filled<br>Blank contamination[2] |
| July 19, 2004 | <70 | NA | Blank contamination |
| July 23, 2004 | <39 | NA | |
| July 26, 2004 | <30 | NA | |
| July 30, 2004 | 69 | 21 | |
| Aug 2, 2004 | <22 | NA | |
| Aug 6, 2004 | <59 | NA | Tank spiked[3] |
| Aug 9, 2004 | <24 | NA | Tank filled |
| Aug 13, 2004 | <142 | NA | |
| Aug 16, 2004 | <137 | NA | |
| Aug 20, 2004 | <147 | NA | |
| Aug. 23, 2004 | <200 | NA | |
| Aug 27, 2004 | <199 | NA | |
| Aug 30, 2004 | <187 | NA | |
| Sept 3, 2004 | <92 | NA | Tank filled |
| Sept 6, 2004 | <89 | NA | |
| Sept 10, 2004 | <67 | NA | |
| Sept 13, 2004 | <126 | NA | |
| Sept 17, 2004 | <90 | 36 | Tank filled |
| Sept 20, 2004 | <86 | 28 | |
| Sept 24, 2004 | <29 | NA | |
| Sept 27, 2004 | 48 | NA | |
| Oct 1, 2004 | <21 | NA | |
| Oct 4, 2004 | <46 | NA | Blank contamination |
| Oct 8, 2004 | <4.4 | NA | Blank contamination |

[1] Not applicable; NDMA precursor concentration below detection limit.

[2] Blank contained NDMA precursors at a concentration equal to or greater than 50% of the measured NDMA precursor concentration.

[3] On August 6, 2004, approximately 4000 L of tap water spiked with 800 ng of NDMA/L was added to the tanks because the scheduled shipment did not arrive on time. The spiked water was used for two irrigation cycles.

### 4.3.2 NDMA and NDMA Precursors in Leachate

From June 14 through October 12, 2004, leachate from each test plot was sampled on a total of 50 occasions, at a frequency of three samples per week. NDMA was detected in only 9 of the 400 samples (Figures 4.1 and 4.2). In other words, fewer than 3% of the leachate samples contained NDMA at concentrations above the method detection limit of 2 ng/L. The highest concentration of NDMA detected in the leachate samples was 5 ng/L. Analysis of split samples by the City of Long Beach laboratory confirmed the absence of NDMA in the leachate samples. The analytical technique employed by UC Berkeley was less sensitive than the methods used by UC Riverside and the City of Long Beach. Nonetheless, UC Berkeley obtained similar results, with the absence of NDMA in more than 75% of the samples. It is difficult to determine if the low concentrations of NDMA (i.e., <100 ng/L) detected by UC Berkeley in the remaining samples were attributable to contamination that occurred during sample processing.

The leachate samples indicate that NDMA was not transported into the deep soil layer when NDMA-containing wastewater effluent was used for irrigating the turfgrass. Given that the NDMA concentration in the input water was relatively high and that very high irrigation rates were used, the lack of NDMA appearance in the leachate suggests that the turfgrass plots were highly effective in preventing NDMA from leaching through the soil profile. Furthermore, the transport of NDMA should have been facilitated by the use of sandy textured soils that contained little organic matter below the surface layer of turf. Under these conditions, which were very conducive to NDMA transport, NDMA in the wastewater effluent did not reach the groundwater.

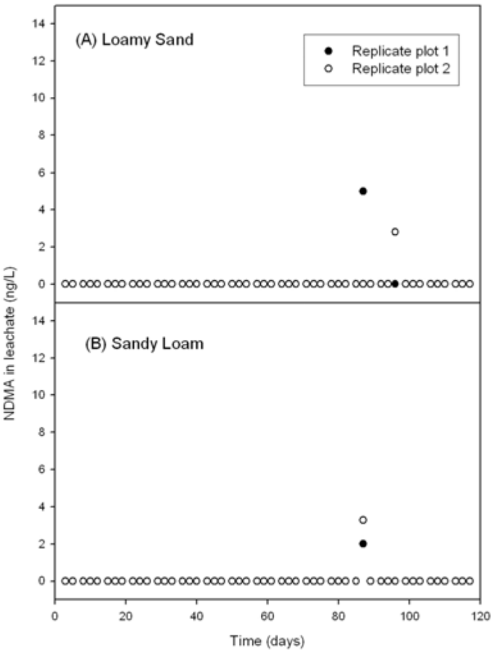


**Figure 4.1. NDMA Concentrations in Leachate from Turfgrass Plots Irrigated with Wastewater Effluent in the Morning. (A) Loamy sand plots; (B) sandy loam plots.**

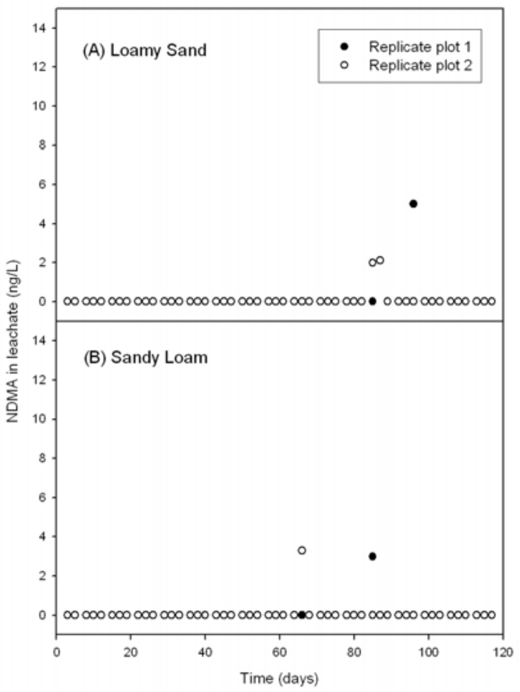


**Figure 4.2. NDMA Concentrations in Leachate from Turfgrass Plots Irrigated with Wastewater Effluent in the Evening. (A) Loamy sand plots; (B) sandy loam plots.**

The concentrations of NDMA precursors in the leachate also were low, with precursors detected in only 8 of the 140 samples analyzed (Figures 4.3 and 4.4). The absence of NDMA precursors in the leachate samples is consistent with the low concentrations of precursors detected in the wastewater effluent samples. Furthermore, NDMA precursors are not present at elevated concentrations in natural organic matter produced by decomposition of organic matter derived from plants (Gerecke and Sedlak, 2003).

## 4.4 NDMA LOSS PATHWAYS IN TURFGRASS SYSTEMS

The absence of NDMA in leachate may be attributable to one or more of the following loss mechanisms: (1) NDMA was rapidly degraded in the soil; (2) NDMA was rapidly taken up by the plant; and (3) NDMA was rapidly lost from the soil by gaseous-phase diffusion and emission from the surface. To better understand the reasons why NDMA was not detected in the leachate from the turfgrass plots, two additional experiments were carried out using soils from the field site.

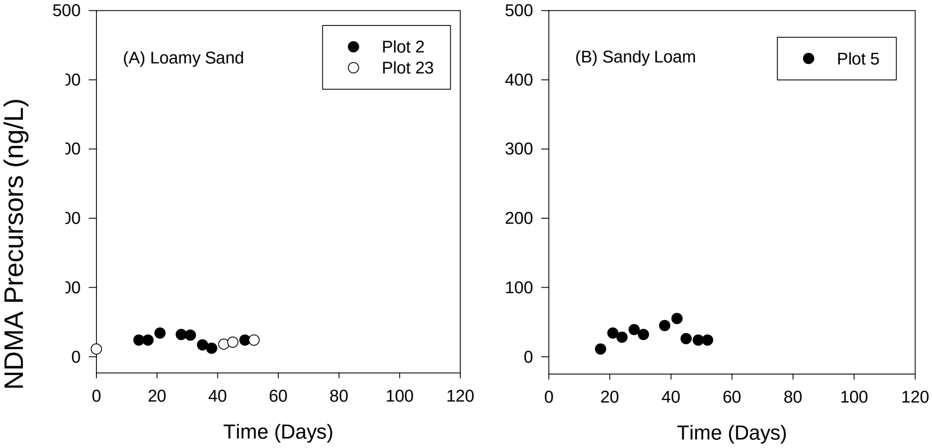


**Figure 4.3. NDMA Precursor Concentrations in Leachate from Turfgrass Plots Irrigated with Wastewater Effluent in the Morning. (A) Loamy sand plots; (B) sandy loam plots.**

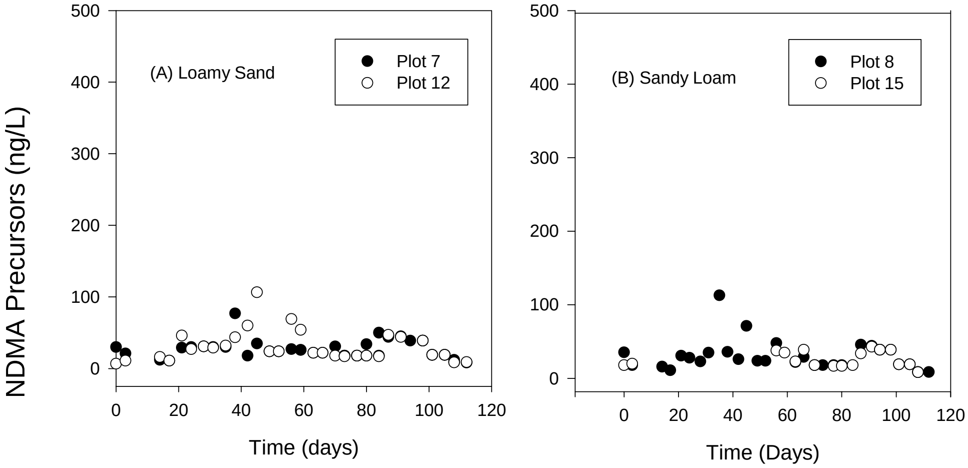


**Figure 4.4. NDMA Precursor Concentrations in Leachate from Turfgrass Plots Irrigated with Wastewater Effluent in the Evening. (A) Loamy sand plots; (B) sandy loam plots.**

### 4.4.1 NDMA Degradation in Turfgrass Soils

Following completion of the field study, soil samples were taken with an auger from the wastewater irrigated plots and regular plots, and NDMA degradation rates in these soils were determined by using an approach similar to that described in section 3.2. Briefly, soil samples were collected from plots that were irrigated with the tertiary treated wastewater effluent or regular water at depths of 0–10, 10–20, and 20–30 cm. These samples were passed through a 2-mm sieve after slight air drying. The initial water content of the soil samples was adjusted to 10% (w/w) by adding deionized water. Ten grams (dry weight equivalent) of soil was weighed into 125-mL glass serum bottles (Wheaton, Millville, NJ) and spiked with 0.5 mL of 2-mg/L NDMA aqueous solution to give an initial NDMA concentration of 100 µg/kg. The spiked samples were immediately closed by capping with aluminum seals and Teflon-lined butyl rubber septa and were mixed thoroughly by shaking with hand. The sample bottles' contents were incubated in the dark at room temperature (21 °C), and triplicate samples were removed 0, 3, 7, 14, 21, 28, and 56 days after the treatment. For extraction, each soil sample was spiked with 0.1 mL of $d_6$-NDMA in dichloromethane (10 mg/L) and then extracted with 50 mL of dichloromethane by shaking at high speed for 4 h. The solvent extract was filtered through a funnel containing 20 g of anhydrous sodium sulfate, and the dried extract was concentrated to a final volume of about 1 mL under a stream of dry nitrogen. An aliquot of the final extract was used for analysis by GC-MS using the same conditions as described above.

The dependence of NDMA concentration in soil as a function of time was fitted to a first-order decay model to estimate the degradation rate constant ($k$) and half-life ($T_{1/2}$) (Table 4.3). There was little or no difference in NDMA degradation rates between the two soil types. Irrigation with treated wastewater for 4 months did not enhance the soil's ability to degrade NDMA. NDMA degradation in the soil was fastest in the surface layers, with lower rates observed in the layer from 20 to 30 cm. The rate of degradation in the surface layer (0–10 cm) was higher than or similar to that measured for landscape soils with a turfgrass cover (Tables 3.4 to 3.6). It is well known that the thatch layer (i.e., the matted layer consisting of plant debris and fibrous roots) typically contains more organic matter than do the underlying layers. NDMA degradation in the thatch layer could be even faster than observed in the soil samples used in this study. However, as the water infiltration rate was expected to be very high in the turfgrass plots, NDMA in irrigation water should have penetrated readily into the subsurface soil. Therefore, it was unlikely that biodegradation alone accounted for all the loss of NDMA from the soil profile in the field–plot study. Nevertheless, biodegradation, especially near the surface, could be a significant loss pathway for NDMA when it was introduced in turfgrass systems via irrigation.

**Table 4.3. First-Order Constants for NDMA Degradation in Turfgrass Soils**

| Soil sample | $k$ (days$^{-1}$) | $T_{1/2}$ (days) | $r^2$ |
|---|---|---|---|
| | **Soils irrigated with NDMA-containing wastewater** | | |
| Sandy loam | | | |
| 0–10 cm | 0.62 ± 0.102 | 1.1 | 0.92 |
| 10–20 cm | 0.113 ± 0.017 | 6.1 | 0.90 |
| 20–30 cm | 0.052 ± 0.007 | 13.3 | 0.90 |
| Loamy sand | | | |
| 0–10 cm | 0.170 ± 0.027 | 5.0 | 0.90 |
| 10–20 cm | 0.124 ± 0.015 | 5.6 | 0.93 |
| 20–30 cm | 0.0117 ± 0.003 | 59.2 | 0.40 |
| | **Soils irrigated with regular water** | | |
| Sandy loam | | | |
| 0–10 cm | 0.225 ± 0.021 | 3.1 | 0.97 |
| 10–20 cm | 0.122 ± 0.014 | 5.7 | 0.94 |
| 20–30 cm | 0.070 ± 0.010 | 9.9 | 0.88 |
| Loamy sand | | | |
| 0–10 cm | 0.209 ± 0.017 | 3.3 | 0.97 |
| 10–20 cm | 0.13 ± 0.011 | 5.3 | 0.97 |
| 20–30 cm | 0.053 ± 0.007 | 13.1 | 087 |

### 4.4.2 NDMA Degradation in Turfgrass Soils $^{14}$C-NDMA Dissipation in In situ Lysimeters

Following the field–plot study, we also conducted a lysimeter experiment using $^{14}$C-labeled NDMA to understand why NDMA dissipated rapidly in the turfgrass plots. About 10 months prior to the experiment, galvanized aluminum tubes (5 cm [i.d.] by 30 cm [length]) were inserted into the turf plots and allowed to acclimatize under field conditions. *N*-(Methyl-$^{14}$C)NDMA (57 mCi/mmol; >99% pure) was purchased from Moravek Biochemicals (Brea, CA). For treatment, $^{14}$C-NDMA was dissolved in water, and 50 mL of the solution at 10,000 dpm/mL (and 100-µg/L inactive NDMA) was uniformly applied to each lysimeter on October 5, 2004. The plots containing the treated lysimeters were irrigated three times a week with regular water. Three lysimeters for each soil type were removed at 0, 4, 8, and 12 h and 3, 7, 14, 21, and 28 days after $^{14}$C-NDMA treatment. The ends of the soil column were immediately capped with adhesive aluminum foil and stored in a freezer at –20 °C until extraction. For extraction, the frozen soil column was cut into 0–5-, 5–10-, 10–20-, and 20–30-cm increments. Plant and roots were carefully separated from soil, washed with distilled water, and cut into small pieces. The soil contained in each segment was weighed and mixed. Aliquots of the soil and plant samples were removed for determination of water content. The whole plant sample and 40.0 g of wet soil from each increment were individually placed in Soxhlet extraction cups, spiked with 0.1 ml of 10-mg/L $d_6$-NDMA as surrogate, and extracted with 300 mL of dichloromethane for 8 h. The extract was passed through anhydrous sodium sulfate and condensed to 10 mL on a vacuumed rotary evaporator. Duplicates of a 0.5-mL aliquot of the extract were mixed in 6 mL of Ultima Gold scintillation cocktail (Packard Bioscience) and measured for $^{14}$C radioactivity by a Beckman LS 1800 scintillation counter. Following solvent extraction, $^{14}$C associated with the extracted sample matrix was also determined by combusting 50 mg of air-dried plant tissues or 1.0 g of air-dried soil on an R. J. Harvey OX-500 Biological Oxidizer. The evolved $^{14}CO_2$ was trapped in a basic solution, and the activity was measured by liquid scintillation counter. The $^{14}C$ activities from the solvent extract and the extracted sample residues were combined to approximate NDMA levels in samples. However, as the above procedures did not distinguish NDMA from its potential metabolites, the measured $^{14}C$ activity would be an overestimation of the actual NDMA concentration if degradation resulted in formation of $^{14}C$-labeled metabolites. Therefore, information from $^{14}C$ activity would serve as a conservative estimate for NDMA behavior.

The vertical distribution of total $^{14}C$ activity (extractable and nonextractable activity) in in situ lysimeters is shown in Table 4.4 for the sandy loam soil and in Table 4.5 for loamy sand soil. When the soil and plant tissues were extracted immediately after treatment, ≥80% of the added activity was found in the lysimeter, indicating good recoveries by the procedures used. Most of the radioactivity was detected in the top 10 cm of the soil profile. The application of 50 mL in each lysimeter was equivalent to 2.5-cm irrigation, which was about five times the average daily ETo (4.9 mm) and therefore represented a heavier-than-normal irrigation event. The total $^{14}C$ activity rapidly dissipated from the lysimeters, and in 4 h, only 19% was left in the sandy loam soil lysimeters and 26% in the loamy sand soil lysimeters (Tables 4.4 and 4.5). The first irrigation event did not occur until about 18 h after the treatment. On the basis of these results, we conclude that the relatively rapid dissipation of $^{14}C$ from the soil lysimeters was not attributable to leaching. After 28 h, the total activity in each lysimeter decreased to 3.3% for the sandy loam soil and 12.8% for the loamy sand soil. After 3 days, the total activity in each lysimeter was negligible. The decrease of total $^{14}C$ activity as a function of time is also shown in Figure 4.5. The dissipation of solvent-extractable $^{14}C$ activity is depicted in Figure 4.6. Although trace amounts of $^{14}C$ remained in the lysimeters after 3 days, it is clear that nearly all the activity was associated with the sample matrix after extraction and may be considered bound residues (Figure 4.6). After 3 days, the majority of the remaining activity in the lysimeter was recovered from plant tissues, where the $^{14}C$ was mostly in the form of bound residues. Throughout the experiment, the smallest fraction of $^{14}C$ was always found in the 20–30-cm layer. This suggests that irrigation did not cause significant breakthrough of $^{14}C$-NDMA in the 30-cm-long lysimeter. There was no difference in the distribution of radioactivity or the rate of dissipation between the two soil types.

**Table 4.4. Distribution of $^{14}$C Activity in In Situ Lysimeters of Turfgrass Soil after $^{14}$C-NDMA Treatment[1]**

| | Time after $^{14}$C-NDMA application | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | **0** | **4 h** | **8 h** | **12 h** | **28 h** | **72 h** | **168 h** | **336 h** |
| Plant tissue | 0.60 ± 0.22 | 1.65 ± 0.66 | 0.45 ± 0.22 | 1.25 ± 0.06 | 0.74 ± 0.27 | 0.96 ± 0.71 | 0.90 ± 0.37 | 0.98 ± 0.62 |
| 0–5 cm | 28.84 ± 1.46 | 15.82 ± 7.70 | 3.01 ± 2.33 | 4.86 ± 0.64 | 1.70 ± 0.27 | 0.60 ± 0.05 | 0.25 ± 0.27 | 0.42 ± 0.34 |
| 5–10 cm | 39.95 ± 6.41 | 1.58 ± 1.20 | 3.06 ± 4.09 | 2.45 ± 2.80 | 0.71 ± 0.64 | 0.02 ± 0.02 | 0.08 ± 0.11 | 0.14 ± 0.20 |
| 10–20 cm | 10.25 ± 2.07 | 0.10 ± 0.16 | 1.79 ± 2.70 | 0.53 ± 0.52 | 0.15 ± 0.12 | 0 | 0.12 ± 0.03 | 0.04 ± 0.06 |
| 20–30 cm | 0.23 ± 0.13 | 0.02 ± 0.02 | 0.16 ± 0.13 | 0.16 ± 0.09 | 0.05 ± 0.07 | 0 | 0.53 ± 0.39 | 0.01 ± 0.01 |
| **Total** | 79.87 ± 2.95 | 19.14 ± 9.00 | 8.47 ± 4.67 | 9.26 ± 2.71 | 3.32 ± 1.20 | 1.49 ± 0.82 | 1.88 ± 0.76 | 1.55 ± 1.29 |

[1] Sandy loam soil; values are % of applied activity ± standard deviation; *n* = 3.

**Table 4.5. Distribution of $^{14}$C Activity in In Situ Lysimeters of Turfgrass Soil after $^{14}$C-NDMA Treatment[1]**

| | Time after $^{14}$C-NDMA application | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | **0** | **4 h** | **8 h** | **12 h** | **28 h** | **72 h** | **168 h** | **336 h** |
| Plant tissue | 0.48 ± 0.22 | 0.96 ± 0.27 | 0.81 ± 0.44 | 1.36 ± 0.37 | 0.07 ± 0.10 | 1.20 ± 0.47 | 2.85 ± 0.82 | 1.17 ± 0.36 |
| 0–5 cm | 56.51 ± 5.11 | 13.63 ± 12.7 | 7.78 ± 1.33 | 10.12 ± 4.94 | 1.95 ± 0.68 | 0.51 ± 0.16 | 0.56 ± 0.11 | 0.70 ± 0.03 |
| 5–10 cm | 17.79 ± 1.20 | 9.02 ± 10.4 | 0.61 ± 0.29 | 0.97 ± 0.66 | 5.29 ± 0.50 | 0.06 ± 0.08 | 0.13 ± 0.04 | 0.33 ± 0.15 |
| 10–20 cm | 9.24 ± 0.56 | 2.29 ± 3.12 | 0.08 ± 0.11 | 0.16 ± 0.27 | 5.12 ± 6.16 | 0 | 0 | 0.11 ± 0.15 |
| 20–30 cm | 2.80 ± 1.69 | 0.23 ± 0.18 | 0 | 0.03 ± 0.03 | 0.33 ± 0.16 | 0 | 0 | 0.09 ± 0.12 |
| **Total** | 86.83 ± 5.95 | 26.13 ± 10.4 | 9.27 ± 1.51 | 12.62 ± 4.65 | 12.77 ± 6.18 | 1.75 ± 0.38 | 2.81 ± 0.43 | 2.35 ± 0.88 |

[1] Loamy sand soil; values are % of applied activity ± standard deviation; *n* = 3.

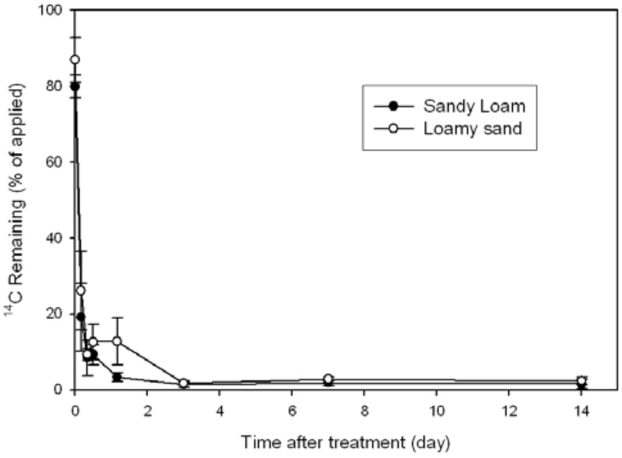


**Figure 4.5. Dissipation of Total $^{14}$C Activity in In Situ Soil Lysimeters**

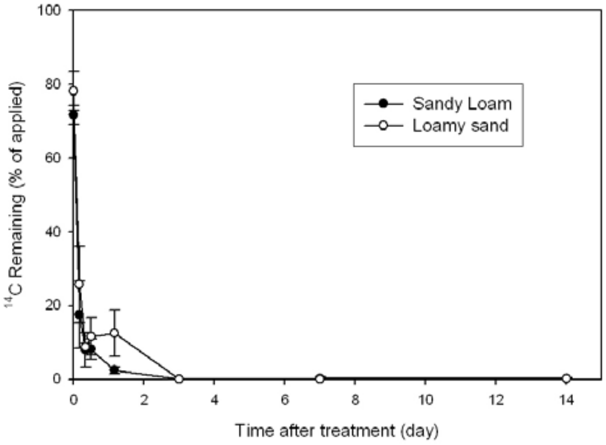


**Figure 4.6. Dissipation of Extractable $^{14}$C Activity in In Situ Soil Lysimeters**

## 4.5 DISCUSSION OF NDMA DISSIPATION MECHANISMS

Results from the $^{14}$C in situ lysimeter experiment support the observation of the field–plot study that NDMA was not leached from the soil in appreciable amounts. Given that the irrigation rates used in the field plot study were very high and the sandy soils at the test site were conducive to leaching, we conclude that NDMA is not transported to groundwater efficiently when wastewater effluent is used to irrigate turfgrass systems such as golf courses, parks, or lawns.

NDMA is miscible with water and is not adsorbed strongly by soils, which suggests that NDMA should be transported efficiently through the soil. In column leaching experiments where the soil was completely saturated and the residence time of NDMA in the soil was very short, NDMA was also found to move like chloride (Dean-Raymond and Alexander, 1976).

In small packed columns (1.0 cm [i.d.]. × 45 cm), *N*-nitrosodipropylamine (NDPA) was found to leach readily through the soil (Saunders et al., 1979). After simulated 60-cm rainfall, 88–94% of the added NDPA was recovered in the leachate. It must be noted that, in such test systems, water flow is always in one direction, and as all soil pores are filled with water, gas-phase transport is eliminated. Furthermore, the hydraulic residence times in the column studies were relatively short compared to those encountered in irrigation systems.

The loss mechanisms in unsaturated field soils are likely to be more complicated than those encountered in saturated column studies. The possible loss pathways for NDMA from turfgrass soil during the field–plot study and the $^{14}C$ in situ experiment may include (1) leaching, (2) degradation, (3) plant uptake, and (4) volatilization. As noted in the $^{14}C$ lysimeter experiment, plant uptake of the spiked $^{14}C$ was always very limited, with less than 3% of the overall radioactivity detected in the plants at the conclusion of the experiment. The limited plant uptake was consistent with what was observed by Dean-Raymond and Alexander (1976). The results from the biodegradation experiments reported here and section 3 indicate that NDMA has a short-to-moderate persistence in soil and that the persistence depends on the soil depth. In the 0–20-cm layers, the measured $T_{1/2}$ at 20 °C was around 1–6 days. However, the loss of $^{14}C$ from the same layers under field conditions was much faster than what was observed in the laboratory studies. The rapid loss of radioactivity could have been due to higher rates of biodegradation in the thatch layer, where higher rates of biological activity occur. Alternatively, volatilization of NDMA could also have been an important mechanism for the loss of radioactivity.

The Henry's Law constant ($K_H$) is needed to assess the volatilization of NDMA. A range of values for $K_H$ has been reported: 0.026 Pa $m^3$/mol (Agency for Toxic Substances and Disease Registry, 1989), 0.12 Pa $m^3$/mol (Syracuse Research Corp., 2005), and 3.4 Pa $m^3$/mol (Liteplo et al., 2002). It is commonly assumed that, for compounds with $K_H \geq 0.25$ Pa $m^3$/mol, vapor-phase diffusion dominates and the chemical's movement in unsaturated soil is rapid (Jury et al., 1983). Therefore, NDMA may be transported in the vapor phase within the soil. The vapor-phase transport of NDMA in soil should be further facilitated by its weak adsorption to the solid phase (i.e., limited retardation by the solid phase) and by the relatively high ETo that occurred during the time of the study (i.e., summertime in Riverside).

Previous studies indicate that, when present close to the surface, NDMA readily volatilized from soil (Oliver, 1979; Oliver et al., 1979; Saunders et al., 1979). Oliver (1979) measured volatilization of NDMA, *N*-nitrosodiethylamine (NDEA), and NDPA from packed soil chambers. Volatilization was determined by trapping the vapor of $^{14}C$-labeled nitrosoamines on activated carbon tubes. When NDMA and NDPA were both applied onto the surface in dichloromethane, emission of NDMA appeared to be instantaneous, reaching about 80% within the first few hours. The amount of dichloromethane used for spiking the nitrosoamines was not given by the author, and it is therefore not possible to determine the penetration depth of the applied material. However, it was noted that the soil was maintained at 70% of field capacity, or about 18% water content (w/w), and volatilization therefore occurred from moist soil (Oliver, 1979). In another treatment, $^{14}C$-labeled NDEA was incorporated into the top 7.5 cm of soil, and volatilization was monitored. Although emission was reduced when compared to the surface application, the loss remained significant (21% in 2 days). Volatilization of NDMA after soil incorporation was unfortunately not measured in this study. Given NDMA's lower boiling point (152 °C, compared to 176 °C for NDEA), it may be expected that NDMA volatilization after soil incorporation would be much more extensive than that of NDEA. In a biometer flask incubation experiment, volatilization loss of >50% was observed for NDEA from sterilized soil (Oliver et al., 1979). Saunders et al. (1979) studied leaching of $^{14}C$-NDPA in small glass soil columns (1.0 cm [i.d.] × 32 cm) placed in field soil. The overall dissipation of NDPA occurred at a much lower rate ($T_{1/2} \approx 3$ wks) than that observed for NDMA in this study. However, very little $^{14}C$ activity was found in the 20–30-cm layer, and no $^{14}C$ activity was detected in the leachate that was collected at the bottom of the soil columns.

In unsaturated field soils, transport of volatile or semivolatile compounds may occur via gaseous-phase diffusion through unfilled soil pores. This process is several orders of magnitude faster than liquid-phase diffusion. Following irrigation, water in the surface layer drains into the lower layers, and the surface soil becomes increasingly unsaturated. Under warm conditions, such as those encountered in our test plots, water near the surface also evaporates, which further decreases the water potential in the surface soil. These processes create a water potential gradient that drives the water to move from the subsurface soil toward the soil surface through capillaries. Upward water movement can be especially rapid in sandy textured soil, as there is little matric potential to hold the water to the soil particles. As NDMA is freely miscible in water, it may be expected that, when upward water movement occurs, NDMA is transported with the water upward to the surface, where it may quickly volatilize into the air. In turfgrass systems, the dense vegetation and fibrous roots also undergo active transpiration. Plant transpiration is proportional to the ambient temperature and may serve as a significant means to further facilitate upward water movement. In summer months, ETo (combination of water evaporation from soil and water transpiration by plants) can be especially substantial as indicated by the large ETo values. The active evapotranspiration, along with the relatively high volatility of NDMA, may result in rapid volatilization of NDMA from the turfgrass soil. The strong upward movement and rapid volatilization losses may have effectively prevented NDMA from reaching into the deeper layer or accumulating in the leachate.

# CHAPTER 5

# FATE OF NDMA AND NDMA PRECURSORS IN SATURATED COLUMNS

## 5.1 BACKGROUND

As indicated by the field data reviewed in Chapter 2 and the laboratory studies reported in Chapter 3, NDMA can undergo biodegradation under certain conditions with half-lives ranging from days to weeks. In addition, NDMA has a relatively low affinity for soil surfaces and travels through soil with little retardation. Results from these and other previously published studies suggest that NDMA that reaches saturated groundwater by infiltration or direct injection may undergo biodegradation if biological activity is sufficient and the appropriate enzymatic systems are active. Results presented in Chapter 3 also suggest that NDMA precursors might persist long enough to reach groundwater wells downgradient of sites where water reuse is practiced.

The laboratory experiments described in Chapter 3 were conducted at elevated concentrations of NDMA and under conditions that are different from those that occur in groundwater (e.g., pure cultures of bacteria and elevated concentrations of NDMA). To assess the fate and transport of NDMA and NDMA precursors under conditions encountered in systems where indirect potable reuse is practiced, a series of soil column experiments were conducted. Two sets of saturated columns were operated at Arizona State University (ASU), and another set of columns was operated at the United States Department of Agriculture (USDA) Water Conservation Laboratory. One set of columns at ASU used effluent from the Mesa Northwest WRP (NWWRP) and was operated under anoxic conditions. The other set of columns at ASU used drinking water from the Colorado Aqueduct Project and was operated under aerobic conditions. The columns at the USDA laboratory simulated crop irrigation using reclaimed wastewater. Among these six unsaturated columns, three were planted with Bermuda grass, two were planted with alfalfa, and the sixth column was a control with no vegetation.

## 5.2 MATERIALS AND METHODS

### 5.2.1 Chemicals and Reagents

NDMA was obtained from Aldrich Chemical Company. The $d_6$-NDMA used as an internal standard was obtained from Cambridge Isotopes Laboratories. The Ambersorb 572 resins used for solid-phase extraction of NDMA were obtained from Rohm and Haas. Dichloromethane (analytical grade) was obtained from Mallinckrodt.

### 5.2.2 Column Studies

One set of saturated columns (i.e., Mesa columns) consisted of three columns operated in series with a water travel time of approximately 20 days. All three columns were of identical design constructed of Plexiglas with an approximate 6-day travel time in each column. Each column was 1.5 m long with an i.d. of 12 cm. The columns, reservoirs, and tubing were protected from light to prevent photolysis of NDMA. The columns were filled with a sandy soil from the Agua Fria River basin that had never been exposed to reclaimed waters. The sandy soil had less than 0.1% organic carbon content by weight and had a hydraulic conductivity of 240 ft/day. The columns were operated under saturated conditions in the downflow mode. Influent water (i.e., wastewater effluent from the Mesa treatment plant) was pumped to the first column by using a peristaltic pump, and the water flowed by gravity through the next two columns in series. The Mesa columns were acclimated to effluent from the Mesa Northwest WRP (NWWRP) for several years prior to the initiation of this study. The NWWRP used nitrifying/denitrifying activated sludge followed by filtration prior to spreading on recharge basins. The NWWRP employs chlorine disinfection after filtration for water to be discharged to the Salt River. To minimize the introduction of microbes into the column and to prevent losses of NDMA prior to application to the column, the wastewater effluent was collected after disinfection.

The Mesa columns were operated under anoxic conditions by purging the effluent with nitrogen gas to remove any dissolved oxygen. A flow rate of 0.75 L/day was maintained throughout the study. All reclaimed waters were spiked with a nominal concentration of 1000 ng of NDMA/L, and bromide (~2 mg/L) was periodically added as a tracer.

The second set of saturated columns (i.e., the CAP columns) consisted of three columns connected in series that have been acclimated to Central Arizona Project (CAP) water. This water was used extensively for groundwater recharge at several locations in Arizona, including the Scottsdale Water Campus. These columns were constructed of stainless steel and had a travel time of approximately 20 days, which is similar to that of the Mesa columns. The CAP columns were packed with the same sandy soil used in the Mesa columns and were operated under oxic conditions. The columns were originally designed to simulate flow conditions around an injection well where groundwater velocities decrease with distance from the well. Therefore, the i.d. of each column increased stepwise with 4.4 cm for the first column, 6.6 cm for the second column, and 8.8 cm for the third column. The influent to the CAP columns was spiked with a nominal concentration of 1000 ng of NDMA/L, and bromide (~ 2 mg/L) was periodically added as a tracer.

Samples from the two sets of saturated columns were collected weekly in a beaker covered fully with aluminum foil to prevent exposure to light. These samples were subjected to solid-phase extraction (SPE) as described in section 5.2.3 prior to analysis by GC-MS-MS. In addition, separate 2-L samples were collected in glass bottles, packed on ice, and sent by overnight mail to UC Berkeley, where they were analyzed for NDMA and NDMA precursors by using the methods described in section 4.2. Separate aliquots also were collected and analyzed for pH, conductivity, bromide, dissolved organic carbon (DOC), nitrogen species, dissolved oxygen, and biodegradable organic carbon.

The USDA columns were designed to simulate irrigation and were located in a greenhouse at the USDA Water Conservation Laboratory in Phoenix (Figure 5.1). The columns were constructed of 8 ft of stainless steel with an i.d. of 12 in. The columns were packed with approximately 6 ft of sandy loam obtained from an existing agricultural field that had not used reclaimed water for irrigation. Each column was placed on a scale that continuously monitored changes in mass. The changes in mass were used to determine losses due to evapotranspiration and maintain constant irrigation efficiency in each column. Effluent from the Tolleson municipal wastewater plant was used for irrigation in the USDA columns. Reclaimed water was added to maintain the desired irrigation efficiency in each column; therefore, when ETo's were higher in the summer, the application of reclaimed water was increased. The reclaimed water was exposed to sunlight for 2 h to remove background NDMA prior to spiking with 1000 ng of NDMA/L and 5 mg of Br/L. The NDMA-containing effluent was applied to the columns at night or was applied to columns that were covered to prevent exposure to light as the water percolated into the soils. Of the six columns at USDA, only four produced a suitable volume of sample. The four columns from which samples were collected were column # 2 (irrigation efficiency 50%, alfalfa grass), column #7 (irrigation efficiency 90%, Bermuda grass), column #8 (irrigation efficiency 90%, Bermuda grass), and column #9 (irrigation efficiency 50%, Bermuda grass). Samples were analyzed for NDMA, NDMA precursors and related parameters as described for the saturated columns.

**Figure 5.1. Unsaturated Soil Columns at the USDA Water Conservation Laboratory.**

### 5.2.3 Analytical Methods

NDMA was extracted by SPE by using the method described in section 4.2. Briefly, 10 μL of 2.5-ng/μL $d_6$-NDMA was added to a 1-L sample as an internal standard. Approximately 200 mg of Ambersorb 572 resin was added to the sample followed by stirring for 24 to 48 h. The resins were separated by filtration and allowed to dry for 24 h. Once the resins were completely dried, they were transferred to a glass vial containing approximately 5 mL of dichloromethane. The resins were extracted overnight, and the dichloromethane extract was transferred to a clean glass vial by using a disposable glass Pasteur pipette. The extracts were sent to UC Berkeley for analysis by GC-MS-MS as described in section 3.3.

- NDMA precursors were analyzed by using the method described in section 3.3.

- DOC was analyzed with a combustion analyzer (Shimadzu TOC 5050). The detection limit was 0.4 mg/L.

- Bromide, nitrite, nitrate, chloride, and sulfate were analyzed by ion chromatography, using a Dionex$^{TM}$ ion chromatograph with an eluent consisting of 9 mM sodium bicarbonate buffer.

Biodegradable organic carbon (BDOC) was measured by using 60 mL of biologically active sand incubated with 500-mL samples in 1000-mL amber glass bottles. The biologically active sand was formed by repeatedly exposing the microorganisms for 5-day intervals until the net change in dissolved organic carbon was the same after each exposure. Actual BDOC measurements were done by using 500 mL of sample water and measuring the initial DOC and the residual DOC after 5 days. The BDOC was calculated as the difference between the initial and final DOC concentrations.

## 5.3 RESULTS

### 5.3.1 Mesa Column

Comparison of the concentrations of NDMA in the influent and effluent of the Mesa column suggested that partial NDMA removal occurred as the water passed through the column. Two sets of data are available for evaluating the Mesa column. The first set of data consists of measurements of NDMA concentrations in extracts prepared by ASU. These data are considered adequate for qualitative comparisons only because NDMA and $d_6$-NDMA contamination was observed in the blanks. Despite the uncertainties associated with these data, concentrations of NDMA detected in the effluent (average concentration = 230 ng/L, with a range of 50 to 250 ng/L) were lower than NDMA concentrations measured in the column influent (average concentration = 670 ng/L, with a range of 250 to 1100 ng/L). The second data set consists of measurements made on extracts prepared by UC Berkeley that did not exhibit the same types of QA/QC issues observed in the ASU extracts. These data indicate nearly complete removal of NDMA in the Mesa column (Figure 5.2), with an average influent concentration of 420 ng/L and an average effluent concentration of 80 ng/L. Although these data are compelling, additional sampling of influent and effluent is required to verify the removal of NDMA. These measurements are currently being made and will be completed after conclusion of this project, using funds from other sources.

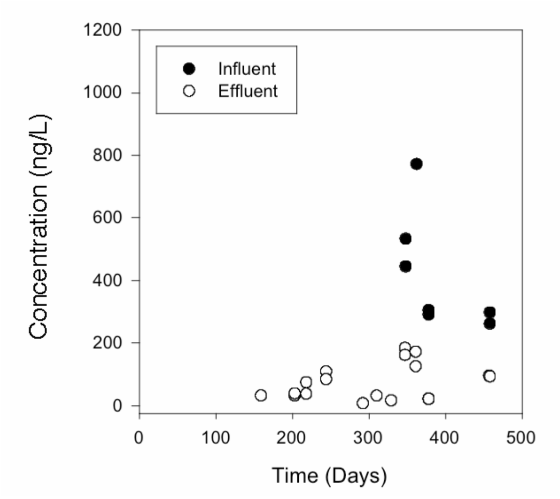


**Figure 5.2. NDMA Concentrations in the Mesa Column.**

The NDMA precursors also appeared to be removed in the Mesa column (Figure 5.3). The average concentration of NDMA precursors in the influent to the column (i.e., 320 ng/L) was higher than the average concentration of NDMA precursors in the column effluent (i.e., 80 ng/L), using the detection limit for the concentration of precursors in the samples in which the precursor concentrations were below the detection limit. The NDMA precursor concentrations in approximately 70% of the effluent samples were below the detection limit, whereas NDMA precursors were always detected in the influent samples.

To assess the biological processes that occurred in the Mesa column, concentrations of DOC and nitrate were measured. The concentrations of DOC decreased from an average of 4.6 mg/L to 2.8 mg/L as the effluent passed through the column (Figure 5.4). These results were consistent with BDOC measurements of approximately 2 mg/L for the Mesa effluent. The similarity between the decrease in DOC as the effluent passed through the column and the BDOC measurement indicates that BDOC was removed during the 18-day travel time in the Mesa column. A mass removal rate of 30 mg of DOC/(day/m$^3$) was calculated for the Mesa columns. A net nitrate decrease of approximately 1.5 mg of N/L was observed throughout the study, and this decrease is consistent with nitrate being used as the primary electron acceptor under anoxic conditions.

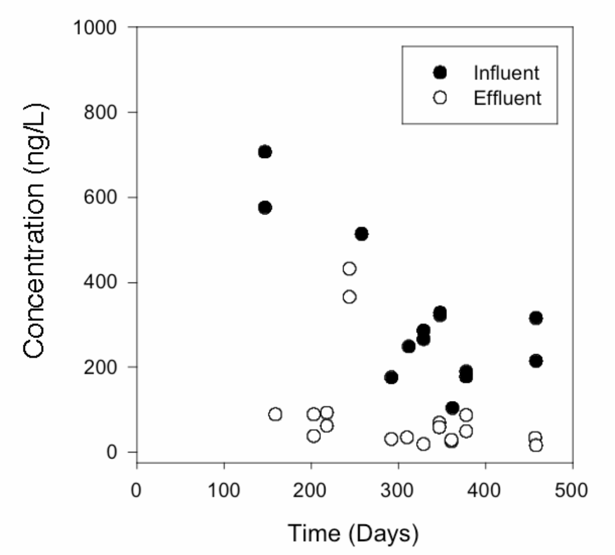


**Figure 5.3. NDMA Precursor Concentrations in the Mesa Column.**

The results for bromide tracer analyses in the Mesa columns are presented in Figure 5.5. The results indicate that plug–flow conditions existed within the columns, with an approximate residence time of 18 days. Within the sampling times used for this study, the dispersion coefficient could not be evaluated, but the failure to detect bromide concentrations between the spiked concentration and the background concentration suggests minimal dispersion. Also, the retention time did not change as the study progressed, and therefore, flow conditions did not change as the consequence of microbial growth or other factors.

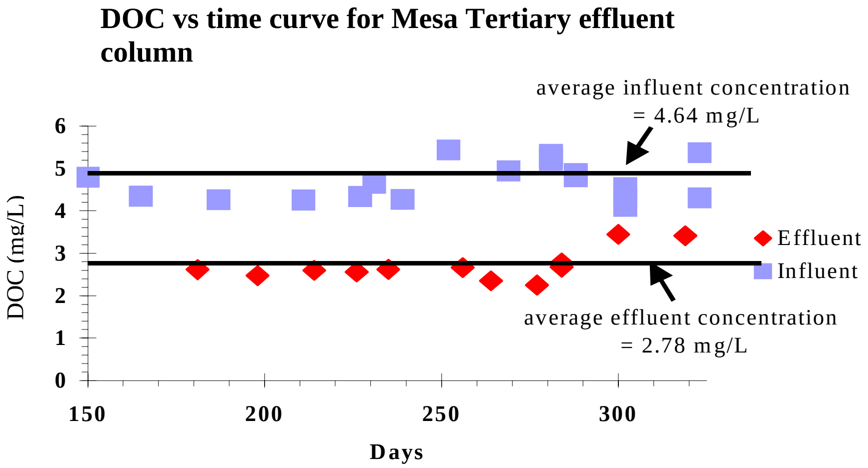


**Figure 5.4. Concentrations of DOC in the Influent and Effluent of the Mesa Column.**

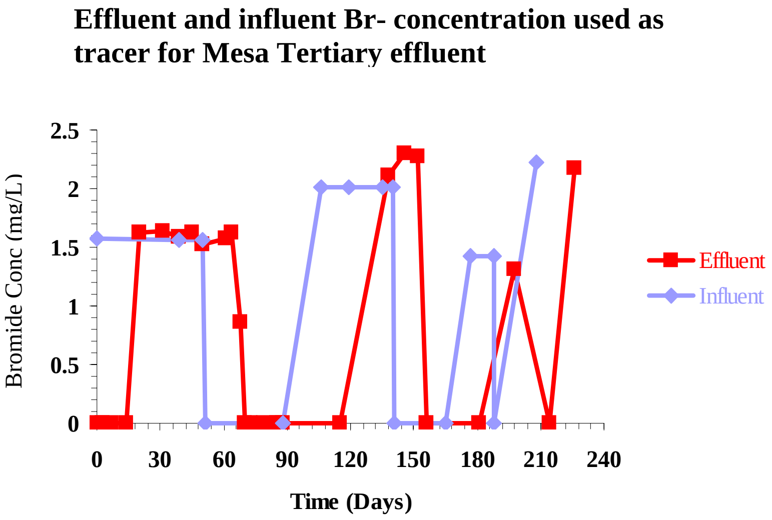


**Figure 5.5. Influent and Effluent Bromide Concentrations for the Mesa Column.**

### 5.3.2 CAP Column

In contrast to the Mesa column, NDMA did not appear to be removed to an appreciable degree in the CAP column (Figure 5.6). As was the case with the Mesa column, two data sets are available for evaluating the CAP column. The ASU data, which were subject to the same concerns as those mentioned for the Mesa column, showed little difference between the influent and effluent NDMA concentrations, with an average influent concentration of 850 ng/L and an average effluent concentration of 1270 ng/L. The data from the UC Berkeley extracts indicated similar results, with an average influent concentration of 420 ng/L and an average effluent concentration of 430 ng/L, after exclusion of an effluent sample that was contaminated with over 7000 ng of NDMA/L.

It was not possible to assess the fate of NDMA precursors in the CAP column because the concentrations of NDMA precursors in five of the six samples from the CAP column were below the detection limit.

The CAP column exhibited less biological activity than did the Mesa column, as evidenced by the decrease in DOC concentrations between the column influent and column effluent (Figure 5.7). The average influent DOC concentration was 3.0 mg/L, while average effluent concentration was 2.5 mg/L. The amount of carbon removed in the column was approximately equal to the BDOC measured in the CAP water (i.e., 0.7 mg/L). The mass removal rate of DOC from the CAP column was estimated to be 6.4 mg of DOC/(day-m$^3$), which is approximately 20% of the DOC mass removal rate observed in the Mesa columns. However, the influent DOC to the CAP column probably had less BDOC than did the influent to the Mesa column.

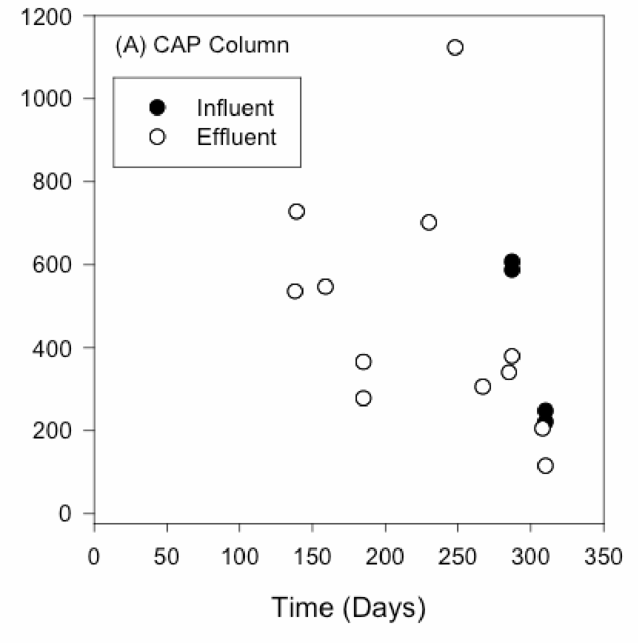


**Figure 5.6. Concentrations of NDMA Detected in the Influent and Effluent of the CAP Column.**

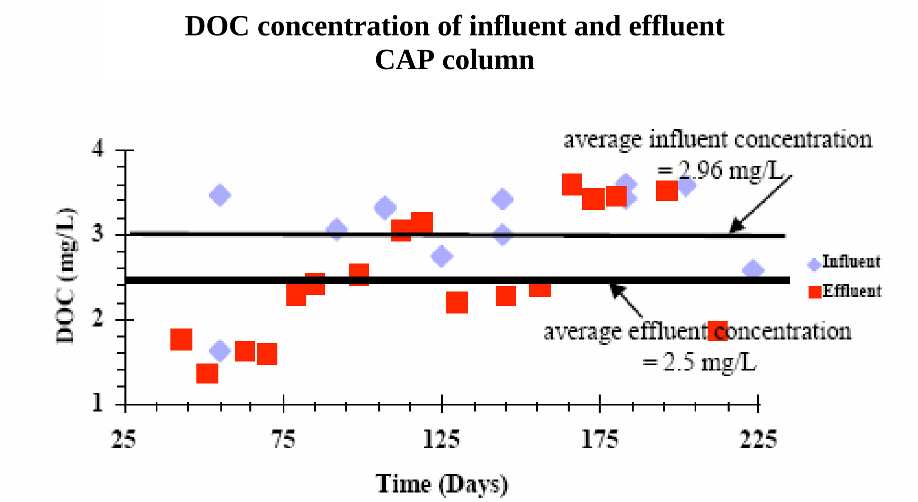


Figure 5.7. DOC Concentrations in the CAP Column.

To ensure that the CAP columns were functioning properly in terms of hydraulics and to accurately assess the retention time for the CAP columns, $Br^-$ was used as a tracer. The concentrations of $Br^-$ in the influent and effluent of the CAP column indicate plug–flow conditions with a retention time of approximately 18 days (Figure 5.8). No apparent changes in flow regime occurred during the time frame of the experiments.

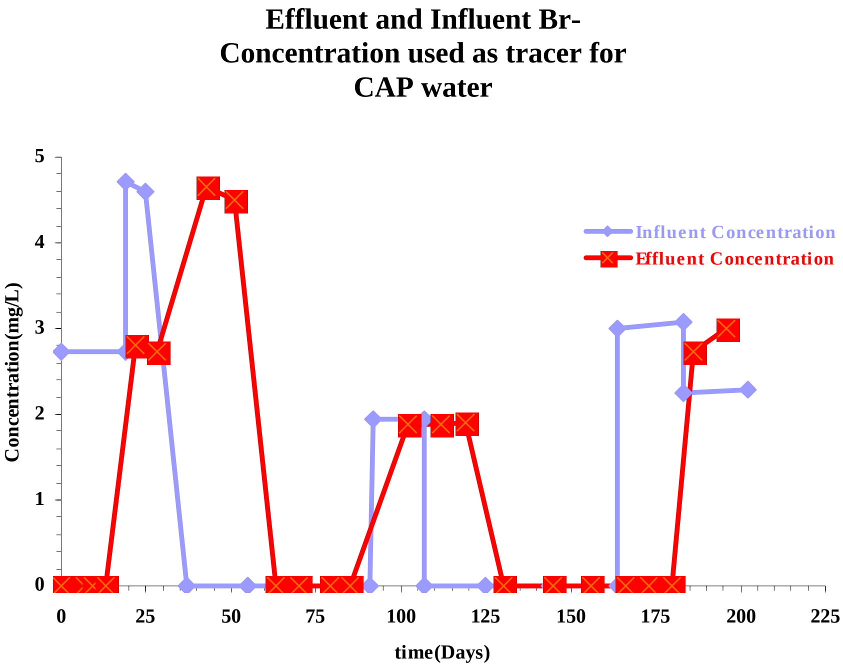


Figure 5.8. Bromide Concentrations in the CAP Column.

### 5.3.3 USDA Columns

NDMA was removed efficiently in the USDA columns. In column 9, i.e., the column run at 50% efficiency with a Bermuda grass cover, NDMA concentrations decreased from an average value of 1260 ng/L in the influent to 298 ng/L in the effluent (Figure 5.9). The concentrations of NDMA in the other columns were not measured due to the limited volume of leachate produced.

To assess the flow conditions in the USDA columns, bromide tracer experiments were conducted. Because the applied quantities of water varied depending upon the ETo and irrigation efficiency, no consistent travel time through the vadose zone was maintained. The breakthrough times for bromide were on the order of months. One hundred days after application began, bromide was observed in the effluent of column 9 (Figure 5.10). As the quantity of water applied was increased during the summer months, breakthrough of the bromide in the columns operated at 70% irrigation efficiency occurred after a period of 150 days. According to the bromide data, the NDMA-amended CAP water had broken through in columns 2, 8, and 9. No data are available for column 7 because the $Br^-$ peak coeluted with other peaks on the ion chromatograph; however, the column was operated under the same conditions as column 2, and therefore breakthrough is suspected to have occurred.

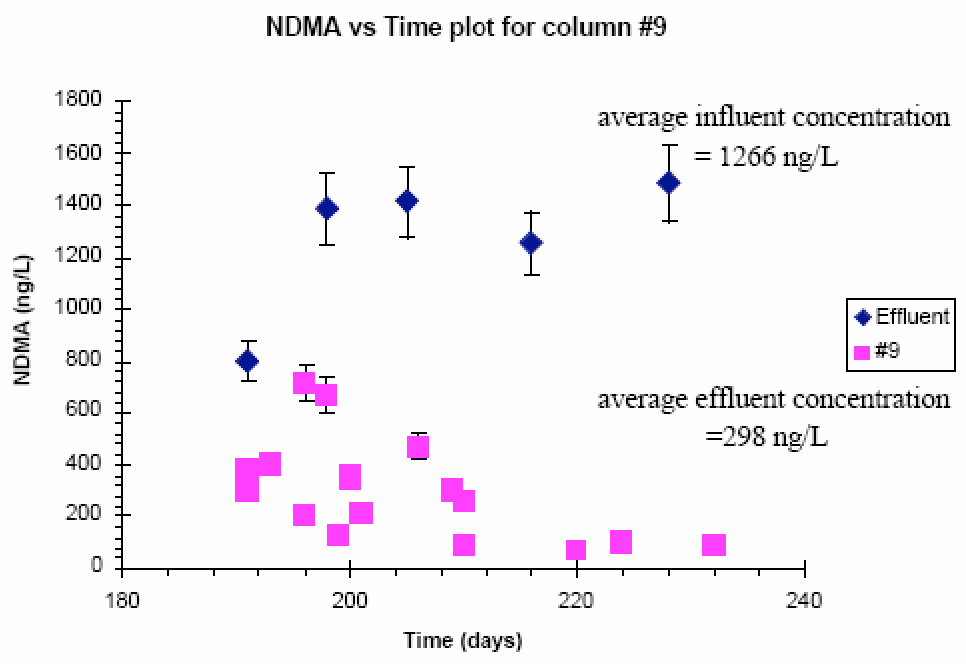


Figure 5.9. NDMA Concentrations in USDA Column 9.

A considerable decrease in DOC was also observed as the water passed through the USDA columns. For example, in column 9 the average influent concentration of DOC was 19 mg/L, while the average DOC concentration in the effluent is 12 mg/L (mass removal rate of 76 mg of DOC/[day-m$^3$] of soil). The BDOC of the Tolleson effluent applied to the USDA columns was significantly greater (i.e., 15 mg of total BDOC/L) than the loss of DOC observed in the USDA column. It is possible that some of the organic carbon detected in the effluent of the USDA columns was derived from the plants and microbes in the column. Nevertheless, it is interesting that the observed mass rates of removal were on the same order of magnitude, although the soil systems are very different. While only limited results were obtained from other USDA columns, similar levels of NDMA removal were observed in all columns independent of irrigation efficiency or crop.

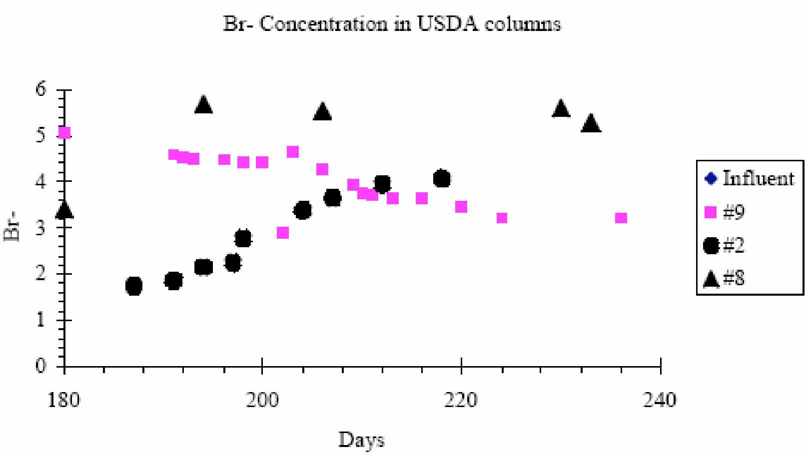


**Figure 5.10. Bromide Concentrations in the Influent and Effluent of the USDA Columns.**

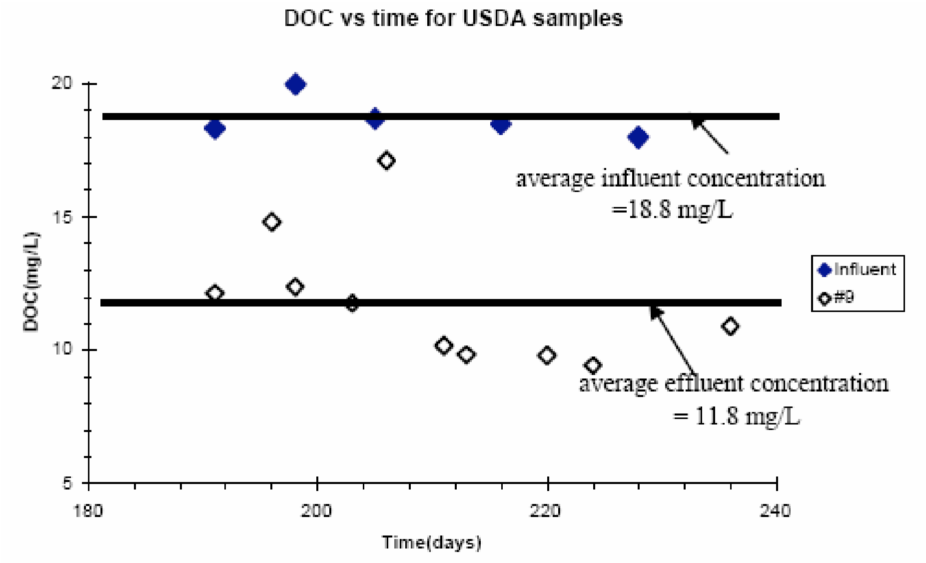


**Figure 5.11. DOC Concentrations in USDA Column 9.**

## 5.4 DISCUSSION OF NDMA AND NDMA PRECURSOR DISSIPATION MECHANISMS

In the saturated columns, NDMA removal appears to have occurred in the Mesa column but not in the CAP column. The key difference between the two columns was the level of BDOC applied to the columns. From these results, it appears that a minimum quantity of BDOC might be necessary to cause enough microbial activity to remove significant concentrations of NDMA via cometabolism. The Mesa tertiary effluent used in the Mesa columns actually had a relatively low concentration of BDOC (~2 mg/L). Many wastewater effluents that are applied to groundwater have a higher concentration of BDOC, and therefore, the degradation of NDMA might occur at higher rates when wastewater effluents with labile DOC are used relative to highly treated effluents or effluents that are subjected to RO.

The results from the Mesa column also indicate that NDMA degradation can occur under anaerobic conditions. These results are contrary to results obtained in pure culture systems (Chapter 3) and indicate that oxygenase enzymes are not the only mechanism through which NDMA degradation can occur.

The results of this study help to explain why NDMA removal has not been observed at sites where effluents are subjected to RO or where wastes from rocket testing are released to groundwater, while NDMA degradation occurs during landscape irrigation and in soil aquifer treatment systems in which wastewater effluent that is rich in carbon is applied (see Chapter 2). However, the results do not explain why NDMA degradation has been observed at the West Basin site, where RO water is injected.

Results from the USDA columns indicate that NDMA removal occurs under unsaturated flow conditions. These results are consistent with findings reported in Chapter 4. However, in the case of the USDA columns, some NDMA was detected in the effluent from the columns, suggesting that the processes operating in the turfgrass plots at UC Riverside were more efficient at removing NDMA than were the processes in the USDA columns. These differences could be related to differences in volatilization and water vapor transport in the two systems.

Results from the Mesa columns indicate that NDMA precursors were removed in the column. The removal of NDMA precursors is surprising because the studies described in Chapter 3 indicate that NDMA precursors are resistant to aerobic biodegradation. Additional research is needed to assess the role of sorption to soil particles and biodegradation under anaerobic conditions.

# CHAPTER 6

# CONCLUSIONS AND RECOMMENDATIONS

Results of the research described in this report indicate that NDMA removal can occur during landscape application of wastewater effluent and when wastewater effluent is applied as part of groundwater recharge systems. A review of field data indicated that sorption was unimportant to NDMA transport and that NDMA biotransformation may occur under certain conditions. Laboratory experiments with pure cultures of bacteria that express monooxygenase enzymes and mixed cultures derived from soils indicate that NDMA undergoes biodegradation on the time scale of hours to days. Experiments conducted in landscape irrigation systems indicate that NDMA is removed as water passes through the unsaturated zone through processes including volatilization and biodegradation. Experiments with saturated columns indicate that NDMA even undergoes partial biodegradation under anaerobic conditions, provided that sufficient amounts of labile organic carbon are present to support active microbial communities.

In contrast to NDMA, precursors that can be converted into NDMA when wastewater effluent is disinfected are resistant to biodegradation. The NDMA precursors are unlikely to degrade under the conditions encountered in effluent-dominated surface waters. However, they appear to be removed in groundwater systems, presumably through sorption to soil particles coupled with slow biodegradation.

These findings suggest that landscape irrigation with wastewater effluent is unlikely to lead to contamination of groundwater under the conditions studied. The concentrations of NDMA in the irrigation water used in our study, which were comparable to the highest concentrations detected in wastewater effluent (e.g., Sedlak et al., 2005), were reduced to levels below the CDHS NL during passage through the vadose zone. The turfgrass plots had a relatively homogeneous soil structure with irrigation rates typical of those used for lawns and golf courses. Additional research would be required to evaluate the potential for higher concentrations of NDMA to reach groundwater through transport in cracks and fractures or when high rates of irrigation are employed in colder climates with lower ETo's.

The results from the saturated column studies suggest that the residual organic matter present in wastewater effluent (i.e., BDOC) plays an important role by supporting an active microbial community that degrades NDMA through cometabolic processes. Thus, it may be possible to augment the rate of NDMA biodegradation in groundwater by providing additional substrates that increase microbial activity. Such an approach is attractive at hazardous waste sites, where NDMA is sometimes released in water that contains few other readily degradable substrates (e.g., deluge water used in the testing of rocket engines). It may also be worthwhile to consider the concentration of labile organic carbon in water reuse programs; the removal of labile organic matter during RO could have the unintended consequence of preventing NDMA degradation. The effect of labile organic carbon on the biotransformation of NDMA may also help to explain the absence of NDMA removal observed at the aerospace testing sites described in Chapter 2, where NDMA was released to groundwater without significant sources of labile organic carbon. Additional research is needed to assess the role of labile organic carbon in the degradation of NDMA and related organic compounds in water reuse systems.

Finally, the disappearance of NDMA precursors in the saturated column study suggests that there is a mechanism through which NDMA precursors are removed in soils. Because NDMA precursors are relatively stable under aerobic conditions, it seems likely that sorption plays a role in the process. Additional research is needed to assess the sorption of NDMA precursors on soils and the role of soil bacteria in NDMA degradation.

# REFERENCES

Aerojet-General Corporation. *Western Groundwater Operable Unit, Remedial Investigation Report;* Sacramento, CA, 2000.

Aerojet-General Corporation. *Technical Memorandum: Evaluation of Perchlorate and N-Nitrosodimethylamine (NDMA) in Groundwater, Aerojet Site—Zone 1 and Western Zone 2 Study Areas;* Sacramento, CA, 1998.

Agency for Toxic Substances and Disease Registry. Toxicological profile for N-nitrosodimethylamine. http://www.atsdr.cdc.gov/toxprofiles/tp141.html.

American Public Health Association. *Standard Methods for Examination of Water and Wastewater;* American Public Health Association, Washington, DC, 1998.

Armesto, X. L.; Canle, M.; Garcia, M. V.; Santaballa, J. A. Aqueous chemistry of N-halo-compounds. *Chem. Soc. Rev.* **1998,** *27*, 453–460.

Black & Veatch; Kennedy/Jenks Consultants; Jones & Stokes; Mactec/Harding ESE. *Advanced Recycled Water Treatment Feasibility Project;* 2004.

Boyle, J. J.; Shann, J. R. The influence of planting and soil characteristics on mineralization of 2,4,5-T in rhizosphere soil. *J. Environ. Qual.* **1998,** *27*, 704–709.

Bradley, P. M.; Carr, S. A.; Baird, R. B.; Chapelle, F. N. Mineralization of *N*-nitrosodimethylamine in soil from a groundwater recharge facility and in pure cultures of *Pseudomonas* sp. *Appl. Environ. Microbiol.*, in press.

Brusseau, G. A.; Tsien, H. C.; Hanson, R. S.; Wackett, L. P. Optimization of trichloroethylene oxidation by methanotrophs and the use of a colorimetric assay to detect soluble methane monooxygenase activity. *Biodegradation* **1990,** *1*, 19–29.

Burns, R. G. *Soil Enzymes;* Academic Press: New York, 1978; pp 345–346.

California Department of Health Services. http://www.dhs.ca.gov/ps/ddwem/chemicals/ndma/NDMAindex.htm (accessed March 1, 2005).

Cares, J. W. Determination of formaldehyde by the chromotropic acid method in the presence of oxides of nitrogen. *Am. Ind. Hyg. Assoc. J.* **1968,** *29*, 405–410.

Carey, F. A. *Organic Chemistry;* McGraw-Hill: New York, 1992.

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

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

CH2M Hill. *Baldwin Park Operable Unit Feasibility Study Report, San Gabriel Basin, Los Angeles County, California, ARCSWEST Remedial Activities at Selected Uncontrolled Hazardous Waste Sites in the Zone of Regions IX and X;* Englewood, CO, 1993.

CH2M Hill. *Draft Statement of Work, Irwindale Azusa Study Area, San Gabriel Areas 1–4, Los Angeles County, California*; Englewood, CO, 1990.

CH2M Hill. *Groundwater Monitoring & Tracer Plan for Recycled Water Injection Operations, West Coast Basin Barrier Project;* Englewood, CO, 2003.

*Coastal Plain of Orange County Groundwater Basin*; California's Groundwater Bulletin 118; California Department of Water Resources: Sacramento, CA, 2004.

Cooper, J. M.; Warman, P. R. Effects of three fertility amendments on soil dehydrogenase activity, organic C and pH. *Can. J. Soil Sci.* **1997,** *77*, 281–283.

CVRWQCB. Unpublished database of Aerojet groundwater monitoring results [CD-ROM], **2004.**

Davisson, M. L.; Eaton, G. F.; Hudson, G. B.; Koester, C. J.; Lawrence Livermore National Laboratory; Munoz-McGovern, L.; Reich, K. West Basin Municipal Water District (WBMWD). Fate and Transport of Recycled Water in Coastal Injection Barriers: Initial Characterization in the West Coast Basin Barrier Project, Los Angeles, California. Presented at the 1999 Annual Water Reuse Research Conference, Monterey, California, June 1999.

Dean-Raymond, D.; Alexander, M. Plant uptake and leaching of dimethylnitrosamine. *Nature* **1976,** *262*, 394–396.

Drever, J. I. *The Geochemistry of Natural Waters,* 2nd ed.; Prentice Hall: Englewood Cliffs, NJ, 1988.

Fishman, A.; Tao, Y.; Wood, T. K. Toluene 3-monooxygenase of *Ralstonia pickettii* PKO1 is a *para*-hydroxylating enzyme. *J. Bacteriol.* **2004,** *186*, 3117–3123.

Formaldehyde by VIS Method: 3500. In *NIOSH Manual of Analytical Methods,* 4th ed.; Eller, P. M., Cassinelli, M. E., Eds., U.S. Government Printing Office: Washington, DC, 1994.

Gan, J.; Zhu, Y.; Wilen, C.; Pittenger, D.; Crowley, D. Effect of planting covers on herbicide persistence in landscape soils. *Environ. Sci. Technol.* **2003,** *37*, 2775–2779.

GeoSyntec Consultants and Todd Engineers. *Summary of Technical Findings, Technical Memorandum No. 21, Azusa Land Reclamation Landfill, Azusa, California;* 1995.

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

Gunnison, D.; Zappi, M. E.; Teeter, C.; Pennington, J. C.; Bajpai, R. Attenuation mechanisms of *N*-nitrosodimethylamine at an operating intercept and treat groundwater remediation system. *J. Hazard. Mater.* **2000,** *73*, 179–197.

Harding Lawson Associates. *Revised Work Plan, Assessment of Emerging Chemicals in the Vadose Zone, Aerojet Azusa Facility, San Gabriel Basin, California;* Denver, CO, 2000.

Howard, P. H.; Boethling, R. S.; Jarvis, W. M.; Michalenko, E. M. *Handbook of Environmental Degradation Rates;* Lewis Publishers: Chelsea, MI, 1991.

ICF Kaiser Engineers. *Scoping Report;* Pittsburgh, PA, 1989.

International Water-Guard. Disinfection of Water by Ultraviolet Light. http://www.waterknowledge.com (accessed May 24, 2004).

Jensen, J. S.; Helz, G. R. Rates of reduction of N-chlorinated peptides by sulfite: relevance to incomplete dechlorination of wastewaters. *Environ. Sci. Technol.* **1998,** *32*, 516–522.

Kaplan, D. L.; Kaplan, A. M. Biodegradation of *N*-nitrosodimethylamine in aqueous and soil systems. *Appl. Environ. Microbiol.* **1985,** *50*, 1077–1086.

Kates, M. Techniques of Lipidology: Isolation, Analysis, and Identification of Lipids. In *Laboratory Techniques in Biochemistry and Molecular Biology;* Burdon, R. H.; Knippenberg, P. H., Eds.; Elsevier: New York, 1986; Vol. 3, pp 106–107, 114–115.

Kroeger-Koepke, M. B.; Koepke, S. R.; McClusky, G. A.; Magee, P. N.; Michejda, C. J. α-Hydroxylation pathway in the in vitro metabolism of carcinogenic nitrosamines: N-nitrosodimethylamine and N-nitroso-N-methylaniline. *Proc. Natl. Acad. Sci. USA* **1981,** *78*, 6489–6493.

Lenntech. *Disinfection by Ultraviolet Light*. http://www.lenntech/will1.htm (accessed May 24, 2004).

Liteplo, R. G.; Meek, M. E.; Windle, W. *N*-Nitrosodimethylamine: Concise International Chemical Assessment Document 38. http://www.inchem.org/documents/cicads/cicads/cicad38.htm (accessed May 12, 2003).

Lyman, W. J.; Reehl, W. F.; Rosenblatt, D. H. *Handbook of Chemical Property Estimation Methods: Environmental Behavior of Organic Compounds;* American Chemical Society: Washington, DC, 1990.

Mallik, M. A. B.; Tesfai, K. Transformation of nitrosamines in soil and in vitro by soil-microorganisms. *Bull. Environ. Contam. Toxicol.* **1981,** *27*, 115–121.

McGovern, L. M.; Dryden, F. D. *West Basin Water Recycling Plant, West Coast Basin Barrier Project Expansion Phase III Amended Engineering Report;* West Basin Municipal Water District: Carson, CA, 2002.

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

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.* **2003a,** *20*, 389–404.

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

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

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

Oliver, J. E. Volatilization of some herbicide-related nitrosamines from soils. *J. Environ. Qual.* **1979,** *8*, 695–701.

Oliver, J. E.; Kearney, P. C.; Kontson, A. Degradation of herbicide-related nitrosamines in aerobic soils. *J. Agric. Food Chem.* **1979,** *27*, 887–891.

Parsons, T.; Maita, Y.; Lalli, C. *A Manual of Chemical and Biological Methods for Seawater Analysis;* Pergamon Press: Elmsford, N.Y., 1984; pp 3–33.

Pehlivanoglu, E.; Sedlak, D. L. Bioavailability of wastewater-derived organic nitrogen to the alga Selenastrum Capricornutum. *Water Res.* **2004,** *38*, 3189–3196.

*Planned Utilization of the Ground Water Basins of the Coastal Plain of Los Angeles County, Appendix A, Ground Water Geology;* California Department of Water Resources: Sacramento, CA, 1961.

*Record of Decision for the Western Groundwater Operable Unit OU-3, Aerojet Sacramento Site, July 20, 2001;* U.S. Environmental Protection Agency, U.S. Government Printing Office: Washington, DC, 2001.

Rowland, I. R.; Grasso P. Bacterial degradation of nitrosamines. *Biochem. Soc. Trans.* **1975,** *3,* 185–188.

Roy F. Weston, Inc. *Remedial Investigation/Feasibility Study, Scoping Document, Aerojet General Corporation*; West Chester, PA, 1984.

Saunders, D. G.; Mosier, J. W.; Gray, J. E.; Loh, A. Distribution, movement, and dissipation of N-nitrosodipropylamine in soil. *J. Agric. Food Chem.* **1979,** *27,* 584–589.

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.

Sharp, J. O.; Wood, T. K.; Alvarez-Cohen, L. Aerobic biodegradation of N-nitrosodimethylamine (NDMA) by axenic bacterial strains. *Biotechnol. Bioeng.* **2005,** *89,* 608–618.

Syracuse Research Corporation. *Dimethylnitrosamine* entry in Chemfate Data Base. http://www.syrres.com/esc/efdb.htm.

Taguchi, V.; Jenkins, S. D. W.; Wang, D. T.; Palmentier, J. P. F. P; Reiner, E. J. 1994. Determination of n-nitrosodimethylamine by isotope-dilution, high-resolution mass-spectrometry. *Can. J. Appl. Spectrosc.* **1994,** *39,* 87–93.

Tao, Y.; Fishman, A.; Bentley, W. E.; Wood, T. K. Oxidation of benzene to phenol, catechol, and 1,2,3-trihydroxybenzene by toluene 4-monooxygenase of *Pseudomonas mendocina* KR1 and toluene 3-monooxygenase of *Ralstonia pickettii* PKO1. *Appl. Environ. Microbiol.* **2004,** *70,* 3814–3820.

Tate, R. L.; Alexander, M. Stability of nitrosamines in samples of lake water, soil, and sewage. *J. Natl. Cancer Inst.* **1975,** *54,* 327–330.

Tate, R.L.; Alexander, M. Resistance of nitrosamines to microbial attack. *J. Environ. Qual.* **1976,** *5,* 131–133.

Tu, Y. Y.; Yang, C. S. Dimethylation and denitrosation of nitrosamines by cytochrome P450 isozymes. *Arch. Biochem. Biophy*s. **1985,** *22,* 32–40.

U.S. Environmental Protection Agency. Office of Research and Development National Center for Environmental Assessment Database. Integrated Risk Information System. http://www.epa.gov/ngispgm3/iris/subst/0045.html (access date?).

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

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.

Yoshinari, T.; Shafer, D. Degradation of dimethyl nitrosamine by Methylosinus trichosporium OB3b. *Can. J. Microbiol.* **1990,** *36*, 834–838.

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