FORMATION STUDIES ON
N-NITROSODIMETHYLAMINE (NDMA) IN NATURAL WATERS

_____

A Dissertation

presented to

the Faculty of the Graduate School

University of Missouri-Columbia

_____

In Partial Fulfillment

of the Requirements for the Degree

Doctor of Philosophy

_____

by

XIANGHUA LUO

Dr. Thomas E. Clevenger, Dissertation Supervisor

DECEMBER 2006

The undersigned appointed by the Dean of the Graduate School, have examined the dissertation entitled

FORMATION STUDIES ON N-NITROSODIMETHYLAMINE (NDMA) IN
NATURAL WATERS

Presented by

Xianghua Luo

A candidate for the degree of

Doctor of Philosophy in Environmental Engineering

And hereby certify that in their opinion it is worthy of acceptance.

_____
Thomas E. Clevenger, Chair

_____
Allen Thompson, outside member

_____
Shankha K. Banerji

_____
John J. Bowders

_____
Kathleen Trauth

DEDICATIONS

This dissertation is dedicated to my husband Xiancheng Fang, my son Roger

Hongbo Fang, my parents Xianbao Luo and Lizhen Jiang, for their love and support.

ACKNOLOGEMENTS

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

FORMATION STUDIES ON

N-NITROSODIMETHYLAMINE (NDMA) IN NATURAL WATERS

Xianghua Luo

Advisor: Thomas E. Clevenger

Abstract

N-nitrosodimethylamine (NDMA), a potential carcinogen, has been reported as a disinfection byproduct associated with the use of chloramines and under certain conditions with chlorine in the drinking water and wastewater treatment plants. As chloramines become used as a primary and post disinfectant instead of chlorine by more water utilities to reduce total trihalomethanes (TTHM) and haloacetic acids (HAAs) formation, the public may be increasing exposed to NDMA. The state of California established action level, a health-based advisory level, of 10 ng/L for NDMA in drinking water.

An analytical method for the measurement of NDMA in waters at the trace level was developed using gas chromatography/mass spectrum with chemical ionization in the mode of selected ion storage coupled with solid phase extraction and liquid-liquid extraction method. NDMA levels in 10 drinking water treatment plants in Missouri were investigated and it was found that NDMA in water samples from four utilities using monochloramine as disinfectant were higher than 10 ng/L.

The NDMA formation in natural waters was explored and data showed that natural organic matter (NOM) played important role in this process. A further study on the natural organic matter from 7 water samples in Missouri showed that the hydrophilic fraction has greater NDMA formation potential than the hydrophobic and transphilic fractions. Among the three fractions of NOM, hydrophobic fraction has the least formation potential. The effect of pH on the formation potential showed that under the basic condition which is close to the operation system in the drinking water utilities in Missouri, the NDMA formation yield would be much higher than under acid conditions and this effect is more obvious with the hydrophilic part of NOM than the other two fractions. The effect of bromide ion in the NDMA formation in natural waters was also determined. It was found that it accelerated the rate of NDMA formation by the two pathways, either via oxidation by monochloramine or free chlorines.

The findings reported in this dissertation provide data on NDMA occurrences in drinking water and natural waters in Missouri. The results provide valuable information about NDMA precursors in natural waters and this information could be used in the further study of mitigating NDMA formation or removing NDMA precursors in drinking water utilities. The results on factors affecting on NDMA formation provide more information for water utilities to determine operation conditions to reduce and control NDMA formation.

CHAPTER 1

INTRODUCTION

Water utilities often use monochloramine instead of free chlorine as a disinfectant because less total trihalomethanes (TTHMs) and haloacetic acids (HAAs) are formed. TTHMs and HAAs are regulated under the Environmental Protection Agency's (EPA's) Stage 1 and Stage 2 Disinfectants and Disinfection Byproducts Rule (USEPA, 2005). A survey performed by the American Water Works Association (Water Quality Division Disinfection Committee, 1992) found that 20% of the surveyed utilities used some form of the chlorine-ammonia process. In water where monochloramine is used in the disinfection process, N-Nitrosodimethylamine (NDMA) is reported to be a disinfection by-product during the chloramination process which could be a health concern for utilities using monochloramine as a disinfectant or using free chlorine as a disinfectant in ammonia containing water systems.

N-nitrosodimethylamine (NDMA) is one of the extremely potent carcinogens, the N-nitrososamines (U.S. EPA, 2002). Its cancer potencies, inhalation/oral slope factor, both 16 (mg/kg· day)$^{-1}$, and the inhalation unit risk of 4.6×10^{-3} (µg/m^3)$^{-1}$, are much higher than those of the trihalomethanes (California Cancer Potency Values, 2002). It has `long been used as an intermediate in the production of 1,1-dimethylhydrazine (UDMH), a storable liquid rocket fuel, and also observed in a variety of foods. It is now mainly released as a by-product and contaminant from various industries and from municipal wastewater treatment plants (California of Department of Health and Safety, 2006; Choi and Valentine, 2002a).

NDMA occurrence, as a water contaminant, especially as a drinking water contaminant, was first observed in municipal drinking water in Ontario, Canada in 1989 (OMEE, 1994). In the U.S., the compound was first detected in drinking water wells near a rocket engine testing facility in Sacramento County, CA in 1998, which used UDMH based rocket fuel (California of Department of Health and Safety, 2006). A Maximum Allowable Concentration (MAC) of 9 ng/L was promulgated in 1992 by the Ontario Ministry of the Environment, Canada (Ontario Ministry of Environment and Energy, 1994). The U.S. EPA reported that 0.7 ng/L NDMA in drinking water resulted in a 10^{-6} risk of contracting cancer (USEPA, 2002) and the California Department of Health and Safety (California of Department of Health and Safety, 2006) established an action level of 10 ng/L for NDMA in drinking water to protect public health in March 2002 (California of Department of Health and Safety, 2006).

NDMA is sensitive to light, especially to ultraviolet light and undergoes relatively rapid photolytic degradation, thus photolysis is the major pathway for the removal of NDMA from water. However, high concentrations of organic substances and suspended matter in the surface water make this photodegradation much slower. The high solubility and low partition coefficient make it possible for NDMA to leach into groundwater.

Analytical methods for NDMA in low-level NDMA water involve concentration extraction followed by gas chromatography/mass spectrometry or gas chromatography with a thermionic detector. The detection limit for the method is about 1000 ng/L water. Analysis by gas chromatography with tandem mass spectrometry in the chemical ionization mode (GC/CI/MS/MS) or gas chromatography with high resolution mass spectrometry

(GC/HRMS) will give much better result with a detection limit of around 1 ng/L but requires large capital investment for the instrument.

Research has been conducted on NDMA formation mechanisms in water and wastewater. The main research focus has been on the mechanism of the reaction of "nitrosating agents", especially nitrite, with various organic nitrogen precursors, and the unsymmetrical dimethylhydrazine (UDMH) (Mitch and Sedlak, 2002; Choi and Valentine, 2002a, 2002b). By either pathway, dimethylamine (DMA) was recognized as the most effective precursor of NDMA. Formation and kinetic models have also been developed (Choi and Valentine, 2002a; Mitch and Sedlak, 2002; Choi and Valentine, 2003; Mitch and Sedlak, 2004; Gerecke and Sedlak, 2003). A major deficiency in these efforts is that the model compounds may not resemble aquatic organic matter. Moreover, research work with DMA showed that the NDMA yields was low, which indicated that DMA may not be the main precursor for NDMA in natural waters (Gerecke and Sedlak, 2003). Characterization of the precursors responsible for NDMA formation during chloramination in natural waters is needed to be investigated.

The overall objective of this study was to investigate the NDMA formation precursors in natural water and elucidate the relationships between characteristics of the organic structures in the natural water and NDMA formation. The specific objectives were established as:

1. Development of an optimal analytical method for determining NDMA in drinking water samples in the parts per trillion range using the existing more common ion trap mass spectrometer with chemical ionization instead of the more expensive high resolution mass spectrometer (HRMS);

2. Determination of the NDMA concentration levels during the chloramination of drinking water in Missouri;

3. Determination of the role of natural organic matter (NOM) and the isolated fractions of NOM in NDMA formation;

4. Examination of the NDMA formation kinetics and pH effects on the NDMA formation from precursors in isolated fractions of water source; and

5. Investigation of the role of bromide ion in NDMA formation in natural waters.

1.1   Dissertation organization

Chapter 2 is a literature review on NDMA, as a disinfectant by-product, involving its properties, applications, occurrences in water, regulations, analytical methods, and current research on NDMA formation.

Chapter 3 introduces all related experimental methods and procedures in this study, including water and solutions preparation, analytical methods on NDMA and monochloramine, NDMA formation reactions, and water sample fractionation.

Experimental results are discussed in chapter 4, 5, 6, and 7 mainly presenting results on development and assessment of NDMA analysis methods, NDMA occurrences in drinking water utilities using monochloramine as primary disinfectant, role of natural organic matter in NDMA formation in natural water, and role of bromide ion in the NDMA formation in natural water. The last chapter is a summary of conclusions and recommendations for future work.

CHAPTER 2

LITERATURE REVIEW

2.1   Introduction

        N-nitrosodimethylamine was determined to be a disinfectant by-product of

monochlormaine (Choi and Valentine, 2002a). In this chapter, a literature review of the study

on disinfection and disinfectants is first introduced. A comprehensive introduction on NDMA

is provided on its chemical properties, applications, occurrences, regulations, available

analytical methods, and current studies on its formation in waters.

2.2   Disinfection by chlorine and chloramines

        By far the most common applicable disinfectant in the world, especially in the United

States, is free chlorine because of its effectiveness against most microorganisms, its ability to

maintain a residual in a distribution system, and its ease of use when compared to other

disinfectants such as combined chlorine (chlorine combined with ammonia), chlorine

dioxide, ozone, and ultra violet light (American Water Works Association, 1997;

Montgomery Watson Harza, 2005). However, free chlorine as a major disinfectant has the

disadvantage of producing disinfection byproducts (DBPs) when organic substances are

present in water. Among the DBPs formed, 4 trihalomethanes (THMs) and 5 haloacetic acids

(HAAs) are regulated under Stage 1 Disinfectant and Disinfection Byproducts Rule (D/DBP

Rule) by the United States Environmental Protection Agency (USEPA, 2006). This fact leads

to the increasing popularity of chloramination, the process of applying combined chlorine,

also known as chloramines, as the disinfectant during the disinfection process to limit DBP

production. During the chloramination process, both free chlorine and ammonia are added either sequentially or simultaneously. Because they are more stable and less reactive compared to free chlorine, chloramines as disinfectants can be maintained as a detectable and persistent residual throughout the distribution system. Case studies indicate common TTHM reductions of 40 to 80 percent when free chlorine is replaced by chloramines and only traces of TTHMs and HAA5s are produced after the disinfection process (Montgomery Watson Harza, 2005).

Free chlorine refers to the total of hypochlorous acid (HOCl) and hypochlorite ions (OCl$^-$) produced from chlorine hydrolysis.

$$Cl_2 + H_2O \rightarrow HOCl + HCl \qquad\qquad\qquad \text{Eqn. 2.1}$$

When ammonium is present in water (usually below 1 mg/L of NH$_3$-N), chlorine reacts successively with ammonia to form three chloramine species as more chlorine is added.

Monochloraime formation: $NH_3 + HOCl \rightarrow NH_2Cl + H_2O$ Eqn. 2.2

Dichloramine formation: $NH_2Cl + HOCl \rightarrow NHCl_2 + H_2O$ Eqn. 2.3

Trichloramine formation: $NHCl_2 + HOCl \rightarrow NCl_3 + H_2O$ Eqn. 2.4
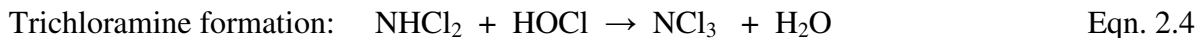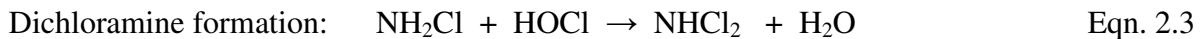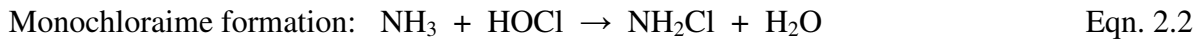
The total of these three reaction products (chloramines) is referred to as combined chlorine. The NH$_3$-N concentrations in water are usually below 1 mg/L and the type of

chloramine formed depends on the pH (Pressley, et al. 1972). Spectrophotometric analyses (Czech et al., 1961; Moore, 1951; Palin, 1952) indicate that the major constituent is monochloramine in the pH range of 7-8.5. As pH decreases below 7, dichloramine appears and increases as pH decreases. Dichloramine is the dominant product in the pH range of 4.5-5.0; below pH 4.0, trichloramine is the predominant product.

Literature shows that monochloramine concentrations reaches a maximum at the 5:1 weight ratio of Cl : NH_3-N (Yutaka, 1967; Pressley et al., 1972). As this weight ratio increases, the disproportionation of monochloramine takes place and forms dichloramine and ammonia are formed (Morris, 1967; Pressley et al., 1972).

$$2NH_2Cl \; \rightarrow \; NHCl_2 \; + \; NH_3 \qquad\qquad \text{Eqn. 2.5}$$

The dichloramine concentration reaches a maximum at the Cl : NH_3-N weight ratio of about 7.5:1 when pH is lower than 7.0. In water with less than 1 mg/L of NH_3-N, this reaction proceeds in competition with monochloramine formation until the chlorine dosage reaches the breakpoint at approximately a 10:1 weight ratio of Cl: NH_3-N (Griffin and Baker, 1941; Pressley et al., 1972). At this point, monochloramine is also believed to be oxidized to nitrogen gas by excess chlorine under slightly alkaline conditions (Cole and Taylor, 1956; Griffin and Chamberlain, 1956; Palin, 1952; Pressley et al., 1972). Other end products including nitrate are also suggested (Chapin, 1931; Corbett et al., 1953; Griffin and Baker, 1941; Palin, 1952; Pressley et al., 1972).

$$2 \, NH_2Cl \; + \; HOCl \;\; \rightarrow \; N_2 \; + 3HCl \; + \; H_2O \qquad\qquad \text{Eqn. 2.6}$$
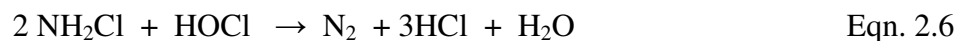
The rate constants from previous studies (Morris, 1967; Moore, 1951; Taras, 1953; Pressley et al., 1972) indicate the formation of monochloramine and dichloramine to be complete well within 1 minute.

2.3   N-Nitrosodimethylamine

N-Nitrosodimethylamine (NDMA) (Chemical Abstracts Service-CAS Registry No. 62-75-9) is one of a group of well known, extremely potent carcinogens, the N-nitrosamines (U.S. EPA, 2002). It is classified as reasonably anticipated to be a human carcinogen (also know as suspect human carcinogen) by the National Toxicology Program (NTP), Department of Health and Human Services and first listed in the Second Annual Report on Carcinogens in 1981 by International Agency for Research on Cancer (International Agency for Research on Cancer, 1978). The EPA integrated risk information service (IRIS) database also classifies NDMA as probably carcinogenic to humans (U.S. EPA, 2002). The Occupational Safety & Health Administration (OSHA) Health Code and Health Effects list the principal effects of exposure to NDMA as cancer and reproductive hazards (teratogenesis or other reproductive impairment) on the organs as liver, kidney, and lungs (Occupational Safety & Health Administration, 2006).

2.3.1 Properties and applications

N-Nitrosodimethylamine (NDMA) is a yellow, volatile, oily liquid of low viscosity that has no distinct odor. It is the simplest dialkylnitrosamine, with a molecular formula of $C_2H_6N_2O$ and a relative molecular mass of 74.08 (ATSDR, 1989) (Figure 2.1). It is soluble in water, alcohol, ether, and many organic solvents and lipids. N-nitrosodimethylamine is combustible, and when heated to decomposition, it emits toxic fumes of nitrogen oxides. It is incompatible with strong oxidizers and strong bases (Hazardous Substances Data Base, 2000; U.S. Department of Health and Human Services, 2005). The compound is sensitive to light, especially ultraviolet light and undergoes relatively rapid photolytic degradation (Polo and Chow, 1976; Sax and Lewis, 1987). However, as NDMA is present in the aqueous environment, it appears to be relatively recalcitrant. NDMA has shown a resistance to degradation in soil, sewage, and lake water (Tate and Alexander, 1975; Greene et al., 1981). No NDMA degradation was found in lake water over a 3.5 month period but the slow disappearance of NDMA was observed in soil, and slow disappearance was observed from sewage with 50% remaining after 14 days (Tate and Alexander, 1975). The physical-chemical properties relevant to the environmental fate of NDMA are listed in Table 2.1.
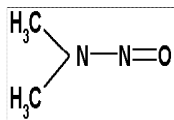
Figure 2.1. Chemical structure of NDMA

Talbe 2.1. Physical and Chemical properties of NDMA. (Siddiqui, 2004)

Parameter	Value
Melting point (°C)	-50
Vapor pressure at 25 °C (mm Hg)	8.1
Boiling point (°C)	150
Henry's law constant at 25 °C (atm·m^3/mol)	$0.4×10^{-4}$
Log Kow at 25 °C	2.15
Saturation concentration (g/m^3)	50
Water solubility, mg/L at 25 °C	500

N-Nitrosodimethylamine is used primarily as a research chemical. Prior to April 1, 1976, the compound was manufactured as an intermediate in the production of 1,1-dimethylhydrazine (also known as unsymmertrical dimethylhydrazine, UDMH), a storable liquid rocket fuel containing approximately 0.1% N-nitrosodimethylamine as an impurity (U.S. Department of Health and Human Services, 2005; Hayes and Stevens, 1970). Other uses of N-nitrosodimethylamine include the control of nematodes, the inhibition of nitrification in soil, as plasticizer for rubber and acrylonitrile polymers, in active metal anode-electrolyte systems (high-energy batteries), in the preparation of thiocarbonyl fluoride polymers, as a solvent in the fiber and plastics industry, as an antioxidant, as a softener of copolymers, and as an additive to lubricants (Sittig, 1985; Merck, 1983).

2.3.2   Occurrences

The primary routes of potential human exposure to N-nitrosodimethylamine are ingestion, inhalation and dermal contact (U.S. Department of Health and Human Services, 2005). There is some potential for occupational exposure for laboratory, copolymer,

lubricant, and pesticide workers. The general population may possibly be exposed to unknown quantities of N-nitrosodimethylamine present in foods and beverages, tobacco smoke, herbicides, pesticides, drinking water, and industrial pollution. Estimates indicate that air, diet, and smoking contribute to potential human exposure at levels of a few micrograms per day (U.S. Department of Health and Human Services, 2005). N-nitrosodimethylamine is present in a variety of foods (Sen et al., 1980; Fine et al., 1977) including cheeses, soybean oil, canned fruit, various meat products, bacon, various cured meats, frankfurters, cooked hams, fish and fish products, spices used for meat curing, apple brandy, beverages and beer (Scanlan et al., 1980), tobacco smoke (Spincer and Westcott, 1976), as well as industrial pollution (Fajen Et al., 1979; Brewer et al., 1980). Concentrations of N-nitrosodimethylamine in the foodstuffs mentioned above have been measured to be between 0 and 85 µg/kg. Average concentrations of NDMA detected in food range from 90 to 100 ng/L for whole milk, 2600 to 2700 ng/kg for bacon, and 300 to 800 ng/kg for cheese (Cerutti and Airoldi, 1996). The U.S. Food and Drug Administration (FDA) and U.S. Consumer Product Safety Commission (CPSC) have determined that N-nitrosodimethylamine is frequently produced during rubber processing and may be present as a contaminant in the final rubber product. N-nitrosodimethylamine has been also typically found in numerous drugs formulated with aminopyrine, including tablets, suppositories, injections, drops, and syrups, at concentrations ranging from < 10 to 371 µg/kg (Kobylinski and Peterman, 1979; Poocharoen et al., 1992; U.S. Department of Health and Human Services, 2005). In tobacco smoke, N-nitrosodimethylamine has been detected at concentrations of 0 to 140 ng/cigarette. Mainstream smoke of nonfiltered cigarettes contained 13 to 65 ng/cigarette, and 5.7 to 43 ng/cigarettes for filtered cigarettes. Sidestream smoke of nonfiltered cigarettes contained 680

to 823 ng/cigarettes, and 1040 to 1770 ng/cigarettes for filtered cigarettes (U.S. Department of Health and Human Services, 2005). An analysis of N-nitrosodimethylamine in smoke-filled bar rooms concentrations of 90 to 240 ng/m^3 while residences contained less than <5 ng/ m^3. A study showed that indoor air polluted with tobacco smoke contained N-nitrosodimethylamine up to 0.24 ng/L (HEEP, 1980).

N-Nitrosodimethylamine is widely spread in the environment. NDMA was detected as an air pollutant in Baltimore, MD, and in Belle, WV (U.S. Department of Health and Human Services, 2005). It was found that the primary source of NDMA in Baltimore was a chemical plant that manufactured 1,1-dimethylhydrazine (UDMH). The concentrations of N-Nitrosodimethylamine at the factory, in adjacent residential neighborhoods, and approximately two miles away in downtown Baltimore were 6,000 to 36,000 ng/m^3, 1,000 ng/m^3, and 100 ng/m^3, respectively. In Belle, WV, the source of the detected NDMA was found to be a chemical factory manufacturing and using dimethylamine while NDMA was a byproduct during the process. Concentrations in downtown Belle and Charleston, WV ranged from 1 to 40 ng/m^3. In chemical factories making or using dimethylamine including plants in New York City, Boston, and New Jersey, similar concentrations of NDMA have been detected.

NDMA has been detected in sea water adjacent to the chemical plant that manufactured 1,1-dimethylhydrazine in Baltimore at concentrations of 0.08 to 0.25 µg/L and in an adjacent sewage treatment facility at 3 µg/L (IARC, 1978; U.S. Department of Health and Human Services, 2005). Industrial wastewater from chemical factories was found to contain 0.2 to 5 µg/L. NDMA has also been found in deionized water, high-nitrate well water, and chlorinated drinking water at concentrations of 0.012 to 0.34 µg/L, < 0.01 µg/L,

and 0.02 to 0.82 µg/L, respectively. NDMA concentrations in soil samples near industrial plants were reported to be 0 to 15.1 ng/g. Dimethylamine-formulated pesticides and herbicides detected NDMA at 190 to 640 mg/L (IARC, 1978; U.S. Department of Health and Human Services, 2005).

NDMA was first detected in municipal drinking water in Ontario, Canada, in 1989. A 9 ng/L health related drinking water objective was established in 1992 by the Ontario Ministry of the Environment (MOE, 1994). In the Drinking Water Surveillance Program (DWSP) in Ontario, Canada, 111 water supply systems were monitored in 1996 and 126 were monitored in 1997. About 11 treatment water samples were reported to exceed the Ontario Drinking Water Objective for NDMA (MOE, 1998).

Much of the recent focus on NDMA as a drinking water contaminant in United States can be traced back to the detection of NDMA in drinking water wells near an aerospace facility that used unsymmetrical dimethylhadrazine (UDMH)-based rocket fuel in Sacramento County, California 1998 (CDHS, 2006). Samples from the drinking water well confirmed the presence of NDMA at the level of 0.15 µg/L. In the same year, NDMA was detected in three drinking water wells in the San Gabriel Basin, California with the concentrations ranging from 0.07 µg/L to 3 µg/L. In 2000, two wells in Orange County, California had NDMA at concentrations of approximately 0.03 to 0.04 µg/L. Also in 2000, a water supply system in Los Angeles County found NDMA in its groundwater sources at the level of 0.032 to 0.076 µg/L which was associated in the past with production of chemicals used in the aerospace industry. Another system in Los Angeles County found NDMA at about 0.03 µg/L which was related to resins used in water treatment for nitrate removal; NDMA concentrations of 0.049 and 0.091 µg/L were found in treated wastewater which was

used as groundwater recharge. A survey on NDMA occurrences in drinking water was conducted on 21 North American drinking water treatment plants from 7 states in US and 4 provinces of Canada from 2001 to 2002. These systems included some pristine sources as well as systems downstream of wastewater treatment plants (Barrett et al., 2003). The results showed that two of them had NDMA at levels higher than 10 ng/L and up to 30 ng/L.

2.3.3   Regulations

U.S. Environmental Protection Agency (USEPA) regulates NDMA under the Resource Conservation and Recovery Act (RCRA) as a constituent of acute hazardous waste (U.S. EPA, 2006) and under the Clean Water Act (CWA) with respect to accidental releases of the compounds (U.S. EPA, 2005b). NDMA is also listed as a Hazardous Air Pollutant to be regulated under the Air Toxics Program in the Clean Air Act (U.S. EPA, 1992). The Superfund Amendments and Reauthorization Act (SARA) identified N-Nitrosodimethylamine as an extremely hazardous substance and establish threshold planning quantities and facility notification responsibilities for state and local emergency response plans. SARA also subjects N-Nitrosodimethylamine to reporting requirements and requires the preparation of its toxicological profile.

U. S. Food and Drug Administration (FDA) established an action level of 5 μg/L of NDMA in malt beverages and 10 μg/L in barley malt (U.S. FDA, 2006). The Occupational Safety & Health Administration (OSHA) promulgated a standard for NDMA that includes requirements for protective clothing, respirators, medical surveillance, and engineering controls (OSHA, 2006). OSHA also regulates NDMA under the Hazard Communication Standard and as a chemical hazard in laboratories (OSHA, 2006).

As mentioned earlier, as N-nitrosodimethylamine was first detected in municipal drinking water in Ontario, Canada, in 1989, a 9 ng/L health related drinking water objective was established in 1992 by the Ontario Ministry of the Environment (MOE, 1994). This objective was changed to a drinking water standard, Interim Maximum Acceptable Concentration, in 2000 (MOE, 2000, 2003).

The USEPA IRIS database classifies NDMA as a probable human carcinogen and lists a drinking water concentration resulting in a 10^{-6} risk of contracting cancer of 0.7 ng/L for NDMA (US EPA, 2002). Since the main concern of the compound is its behavior as an air and food contaminant, EPA has not established any Maximum Contaminant Level (MCL) for it in drinking water.

In 1998, the California Department of Health Service (CDHS) established an action level of 2 ng/L of NDMA in drinking water based on a 10^{-6} cancer risk level to protect public health (CDHS, 2006). The action level is also the notification levels used by CDHS for carcinogenic chemicals. However, analytical capabilities at that time could not detect NDMA levels as low as 2 ng/L, so any detectable quantity was considered to exceed the action level. In 1999, to accommodate studies on NDMA's production in drinking water treatment, CDHS revised the action level to 20 ng/L in drinking water. In 2002, CDHS requested a public health goal (PHG), an early step in the regulatory process involved in developing a drinking water standard, for NDMA from the California Office of Environmental Health Hazard Assessment (OEHHA). As the studies on NDMA's production in drinking water treatment were completed, a revised notification level of NDMA was established at 10 ng/L at the same time (CDHS, 2006). In 2006, OEHHA released a 3 ng/L draft PHG for NDMA in drinking water (OEHHA, 2006).

2.3.4   Analytical methods of NDMA in water

The detection of NDMA in water is a challenge, especially at trace level, because it is a small, neutral, polar molecule and, as such, it is very soluble.

Prior to the recent interest in low-level NDMA occurrence, analysis of NDMA was performed by liquid-liquid extraction and gas chromatography/mass spectrometry (GC/MS) or gas chromatography with a thermionic detector. The detection limit for the method was about 1,000 ng/L (Mitch et al., 2003).

So far, since NDMA is not regulated in drinking water by the US EPA, there is no official method available for measurement of NDMA in drinking water in the parts per trillion (ng/L) range. US EPA method 625 includes NDMA as one of its target analytes in waste water; but the detection limit of the method is 50 ng/L, which is much higher than the current interim regulation limit of 3 ng/L used by CDHS. As NDMA was first reported in drinking water in Canada in 1989 and in California since then, intensive investigations of analytical methods for NDMA in water was initiated. Currently, analysis methods for trace level concentrations of NDMA applied in water involve extraction, preconcentration, and analysis by gas chromatography followed by mass spectrometry, commonly with tandem mass spectrometry in the chemical ionization mode or with high resolution mass spectrometry.

For the first step, liquid-liquid extraction and solid phase extraction are the most common methods to use. Both methods use deuterated NDMA (NDMA-d6) as a surrogate/internal standard in isotopic dilution technique to reduce the uncertainty associated with extraction efficiency. Hence variable recoveries do not represent an insurmountable

16

problem because under the situation of isotopic equilibrium between NDMA-d6 and natural

NDMA, quantification for each sample will be corrected by the recovery. While in the case

that equilibration could not be achieved, quantification can be highly inaccurate.

Furthermore, the quantification is a function of the accuracy of the measurement of the

NDMA-d6, which is directly related to the level of NDMA-d6 added.

Liquid-liquid extraction, a method based on U.S. EPA Method 3510C (U.S. EPA,

1996), extracts samples in 100 ml methylene chloride for consecutively 3 times by the

separatory funnel method at neutral pH. The extracts are then concentrated to 1 ml or less

using rotary evaporators or nitrogen blowdown. The drawback of this method is that

recoveries have been shown to be low and variable, from 10% to 100% and may generate

emulsions that are difficult to handle when used for wastewater effluent samples (Eaton and

Briggs, 2000). Additionally, the extraction for this method is relatively rapid (<1 hour), so

assumption of adequate equilibrium between NDMA and NDMA-d6 may be questionable.

Improvement of extraction efficiency by up to 50% was obtained by adding up to 100 g/L of

sodium chloride (Yoo et al., 2000).

Solid phase extraction has been used to improve extraction efficiency and reduce the

volume of methylene chloride required for the extraction. Carbonaceous resins including

Ambersorb 572 and Ambersorb 348 were used in an NDMA solid phase extraction method

(Jenkins et al., 1995). Among those resins, Ambersorb 572 gave the best extract recovery

which reached approximately 30%.

Other researchers used a carbon-based Empore disk instead of the Ambersorb resin to

extract NDMA at parts-per-trillion (ng/L) concentrations from aqueous samples (Tomkins

and Griest, 1996). The carbon-based Empore disk and an Empore C18 membrane extraction

disk used as reversed-phase to remove nonpolar water-insoluble neutral compounds were preconditioned simultaneously with methanol and water. Aqueous samples were filtered simultaneously through two layered disks under vacuum at ~40-50 mL/min. The carbon-based Empore disk was dried under vacuum and extracted with methylene chloride (dichloromethane). This method gave an extraction recovery of ~64%. However, the manufacturer of the carbon-based Empore extraction disks no longer makes them, so this method is not currently available.

An alternative method, continuous liquid-liquid extraction (CLLE), is based on U.S. EPA method 3520C (U.S. EPA, 1998) and involves extraction of the sample with 100-300 mL methylene chloride under neutral or basic conditions for approximately 6-18 hours. This method avoids problems associated with emulsions in wastewater samples being formed during shaking by separatory funnel extraction, and can yield extraction recoveries of up to 60% (Mitch el al., 2003). The principal disadvantages to the CLLE technique are the more expensive instrumentation and the large volume of water samples required.

Some researchers also have investigated the use of solid phase micro extraction (SPME) for NDMA analysis (Eaton and Briggs, 2000). However, the linearity of NDMA analysis was only shown above 50 ng/L by the SPME method.

Following the extraction, NDMA is separated by a High-Pressure-Liquid-Chromatogram (HPLC), followed by processing through a thermal energy analyzer (TEA) (Fine et al., 1977), a Gas-Liquid-Chromatograph interfaced with a Thermal Energy Analyzer (GLC-TEA) (Kimoto et al., 1981), a capillary gas chromatograph followed by detection by a Nitrogen-Phosphorous detector (NPD) (Andrews and Taguchi, 2000), a chemiluminescent nitrogen detector (Tomkins et al., 1995; 1996), a high-resolution mass spectrometer (Taguchi

et al., 1994), mass spectrometry in the mode of traditional electron impact (EI) with selected ion monitoring (SIM) (Eaton, et al., 2000), or tandem mass spectrometry in the chemical ionization mode (Plomley et al., 1994; Mitch, et al., 2003). The application of NPD has a detection limit of 150 ng/L for NDMA (Siddiqui and Atasi, 2004). Sensitivity and selectivity make high-resolution mass spectrometer and tandem mass spectrometer the most common technique currently used for analysis of low concentrations of NDMA in water. The method applying tandem mass spectrometry using a quadrupole ion-trap mass spectrometer in the chemical ionization mode for the determination of NDMA in water samples has a detection limit of approximate 1.0 ng/L (Plomley et al., 1994; Siddiqui and Atasi, 2004).

Contamination in the blank samples that are free from NDMA is a big issue for analysis of NDMA at trace levels in water. Deionized and distilled water were found to be contaminated with several ng/L of NDMA (Kimoto et al., 1981). Deionized water from a mixed bed ion exchange resin contained high concentrations of NDMA (>20 ng/L), and water from a carbon cartridge (Milli-Q) that did not have a post-cartridge UV irradiation step may contain more NDMA than the feeding water (Andrews and Taguchi, 2000). Including a UV light in the deionized water system could control the contamination in the blank. Purchased HPLC grade water or better quality water provides NDMA-free for blank preparation during the quality assurance process (Andrews and Taguchi, 2000).

Contamination may also come from deuterated NDMA-d6 because this chemical is never more than 98% pure. This could be mitigated by using a low concentration of the NDMA-d6.

Although free chlorine will not lead to any obvious interferences to NDMA analysis under basic conditions, it is critical to dechlorinate water samples for assessing NDMA

19

formation as a disinfection byproduct and the chlorinating reaction should be stopped (Eaton et al., 2000). Residual free chlorine in the sample could be quenched by adding ascorbic acid or sodium thiosulfate (Eaton et al., 2000; Mitch et al., 2003).

2.3.5   Current research on NDMA formation mechanisms

It is generally believed that NDMA is formed through two primary chemical reaction mechanisms: by the nitrosation and by the monochloramine-UDMH pathway. The nitrosation pathway also includes the classical nitrosation, free-chlorine-enhanced nitrosation

2.3.5.1   Classical nitrosation of NDMA

Nitrosation, a reaction between nitrite and common organic nitrogen precursors, is the dominant nitrosamine formation pathway in a variety of matrixes and is generally carried out in an acidic aqueous solution with nitrous acid (HNO_2) or in organic solvents with NOCl, N_2O_3, N_2O_4, $NOBF_4$, or NO-3-nitrocarbazole (Smith, 1966). Nitrosamines can be generally obtained by the nitrosation of secondary amines and, usually with difficulty, by the nitrosation of tertiary amines and N', N'-dialkylhydrazides, the other product being an aldehyde (Smith and Pars, 1959). Nitrosation of secondary amines is important because they are ubiquitous: they occur in food, especially after fermentation or cooking (Lijinsky and Epstein, 1970), fish contains relatively high amounts of dimethylamine, and many drugs and pesticides also contain many secondary amines (Mirvish, 1975). The instability of nitrite (Turney and Wright, 1959) makes it first converted to nitrous acid (pK_a 3.37), which explains why nitrosation is catalyzed by acid. The HNO_2 is then converted to an active nitrosating species, e.g., nitrous anhydride (N_2O_3), nitrosyl thiocyanate (ON-NCS), nitrosyl halide

(NOX), or nitrous acidium ion ($H_2NO_2^+$). Most secondary amines including dimethylamine are nitrosated according to Eqn. 2.7 and Eqn.2.8. The nitrosating agent is N_2O_3, produced from 2 molecules of HNO_2 (Mirvish, 1970, 1975).

$$2HNO_2 \iff N_2O_3 + H_2O \qquad \text{Eqn.2.7}$$

$$(CH_3)_2NH + N_2O_3 \rightarrow (CH_3)_2N \cdot N = O + HNO_2 \qquad \text{Eqn.2.8}$$
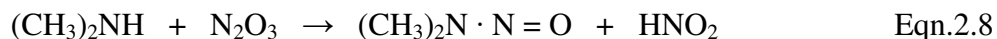
$$\text{Rate} = k_1 [(CH_3)_2NH] [HNO_2]^2 \qquad \text{Eqn.2.9}$$

$$\text{Rate} = k_2 [\text{total dimethylamine}] [\text{total nitrite}]^2 \qquad \text{Eqn.2.10}$$

The rate of nitration is proportional to $[(CH_3)_2NH]$ and $[N_2O_3]$ and hence to $[HNO_2]^2$. In Eqn. 2.9, [nonionized R_2NH] and [free HNO_2] were used, and k_1 should be independent of pH, but [nonionized R_2NH] and [free HNO_2] have to be calculated for each pH. Because the total concentrations of amines and nitrite are used, Eqn. 2.10 is easier, however, the rate constant k_2 varies with pH (Ridd, 1961; Mirvish, 1970). The rate constants k_1 and k_2 for 14 secondary amines and one tertiary amine were determined and the results showed that the ease of nitrosation increased as the basicity of the amine (pK_a) decreased (Sander and Schweinsberg, 1972; Mirvish, 1975). Dimethyleamine (DMA), a determined major and most effective precursor of NDMA, has a pK_a of 10.72 and reaction rate of 0.0017 $M^{-2}s^{-1}$ (Mirvish, 1970, 1975). The reaction rate shows maximum values at pH 3.4 which is the same as the pKa of HNO_2 reflecting the balance between the protonation of nitrite and increased fraction of dimethylamine in the reactive, deprotonated from with increasing pH.

Sander and Schweinsberg (1972) studied the nitrosation of trimethylamine and triethylamine at 100°C. The rate of dialkylnitrosamine formation was at a maximum at a pH

of 3.3 and appeared proportional to [nitrite]^3. A similar maximum pH was found for trimethylamine nitrosation at 100°C (Scanlan et al., 1974) and it is suggested that the formaldehyde which was produced catalyzed the reaction at nonacidic pH values.

This nitrosation mechanism is believed to be responsible for the observed formation of NDMA in vegetables, fish and especially meat products cured with nitrite to prevent the growth of Clostridium botulinum, the bacterium that generates botulism toxin (IARC, 1978; Mitch et al., 2003). Because nitrate can be reduced to nitrite by bacteria in the mouth, it is also very important in the formation of NDMA (Ayanaba and Alexander, 1974; Preussmann, 1984).

While dimethylamine nitrosation in food materials or gastric contents mainly follows Eqn. 2.9 at pH 3.4, it is possible to use Eqn. 2.10 for a rough estimation of NDMA during digestion or storage of food containing dimethylamine and nitrite (Mirvish, 1970). The in vivo nitrosation occurs when nitrite enters the acidic environment of the stomach (Shapley, 1976). The rate constants under various conditions were used to estimate the amount of NDMA expected to be formed in the gastric contents after ingestion of food containing various concentrations of dimethylamine and nitrite and during storage of such food (Mirvish, 1970). It was estimated that, if a man ate a 300 g meal containing 12 mg dimethylamine hydrochloride and 60 mg sodium nitrite, not more than about 3 mg NDMA might be expected to be formed intragastrically.

Nucleophilic anions, especially thiocyanate (a constituent of saliva), enhance the rate of nitrosation through catalytic NDMA formation from nitrite (Fan and Tannenbaum, 1973). The mechanism of nitrosation is different in the absence and presence of thiocyanate, because the proportionality of rate to reactant concentration changes as a function of pH. A

probable mechanism for anion participation was given by Hughes et al. (1958a, b) and Turney and Wright (1959).

$$HNO_2 \; + \; H^+ \; + \; X^- \; \Leftrightarrow \; XNO \; + \; H_2O \qquad\qquad Eqn.2.11$$

$$XNO \; + \; R_2NH \; \rightarrow \; R_2NNO \; + \; H^+ \; + \; X^- \qquad\qquad Eqn.2.12$$
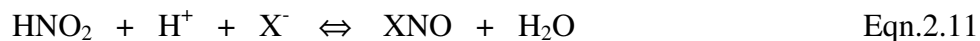
Hence the rate expression for nitrosation with anion present turns out to be

$$d[R_2NNO]/dt \; = \; k'_x[HNO_2][H^+][X^-][R_2NH] \qquad\qquad Eqn.2.13$$

The effectiveness of various anions activeness for nitrosation appeared to be approximately related to their relatively necleophilicity as observed by Hine (1956). The optimum pH for the nitrosation also shifted from 3.4 to 2.3 in the presence of nucleophilic anions (Fan and Tannenbaum, 1973). The overall optimum pH will also depend on the anion concentration.

It is generally assumed that potentially hazardous amounts of N-nitroso compounds cannot be produced unless the interaction of nitrite and amine occurs in an acidic medium (Hawksworth and Hill, 1971; Brooks et al., 1972). However, Keefer and Roller (1973) found that nonenzymatic nitrosation occurred smoothly under neutral and basic conditions in the presence of appropriate catalysts such as formaldehyde, one of the leading industrial products (Kiefer, 1972) and widely distributed in the environment (Fishbein et al., 1970). Significant yields of N-nitrosodimethylamine at room temperature occurred over the pH range from 6.4 to 11.0 in alkaline formaldehyde solutions. Chloral, used as a sedative and anesthetic for

farm animals, and some other aldehydes which are likely to be found in foodstuffs or other environmental components, have been also determined effective catalysts for nitrosation.

N-nitrosodimethylamine was also found to be nitrosated photochemically from dimethylamine in aqueous solution containing nitrite both by the irradiation with a high pressure mercury lamp and by the exposure to sunlight (Ohta et al., 1982). The pH dependency of photochemical formation was examined in the pH range of 6.0 to 10.7. Yields of NDMA after 3 hours irradiation time increased as the pH values increased. The formation of NDMA was enhanced steeply between pH 7 and 8, and changed little above pH 8.

It was also found that fulvic acids had a catalytic effect in the nitrosation process (Weerasooriya and Dissanayake, 1989). Significant quantities of NDMA were formed at pH 5.5 in the presence of fulvic acids.

Ayanaba and Alexander (1974) experimented with sewage samples on reactions between amines including dimethylamine (DMA) and trimethylamine (TMA), which can produce DMA by demethylation, in presence of nitrite or nitrate at pH levels from 4.0 to 7.0. They found NDMA generated at all pH levels tested and higher levels of NDMA were formed from TMA at higher values of pH levels.

2.3.5.2   Free-Chlorine-Enhanced Nitrosation

When free chlorine (HOCl) is present in the solution containing DMA and nitrite, the nitrosation of DMA and formation of NDMA was greatly enhanced. However, the mechanism for the reaction was different from the classical nitrosation (Choi and Valentine, 2003).

NDMA formation by the reaction of DMA with nitrite was studied in the absence and in the presence of HOCl at pH 7. The addition of HOCl greatly enhanced NDMA formation in solutions containing nitrite and DMA in the absence of ammonia. When ammonia is present, the reactions were more complicated as HOCl is added to the solution containing DMA and nitrite. The combination of HOCl and ammonia rapidly forms monochloramine which could also react with DMA to form NDMA. It was found that the source of nitroso group of NDMA formed in the solution in the presence of ammonia and nitrite was both ammonia and nitrite and governed by different mechanisms: free-chlorine-enhanced nitrosation involving nitrite and monochloramine-UDMH pathway involving ammonia which will be discussed in section 2.3.5.3. It was also found that under the situation in the presence of both ammonia and nitrite, free-chlorine-enhanced nitrosation involving nitrite makes a much larger contribution to total NDMA yield than the monochloramine-UDMH mechanism involving ammonia (Choi and Valentine, 2003).

Experiments showed that NDMA formation by the reaction with preformed monochloramine was slow and continuous over 24 hours at pH 7 while the reaction of DMA with nitrite in the presence of HOCl was rapid in the first reaction hour but reached a plateau very quickly (Choi and Valentine, 2003).

The mechanism for this free chlorine existing system may include the hypochlorite oxidation of nitrite which proceeds by Cl^+ transfer from HOCl to NO_2^- to give NO_2Cl (nitryl chloride) as an intermediate (Eqn. 2.14) (Margerum et al., 1978, 1994); then this intermediate nitryl chloride reacts with another nitrite NO_2^- to form dinitrogen tetroxide (N_2O_4) as an intermediate product (Eqn. 2.15) and this reaction is kinetically favorable at neutral pH

25

because the nitrite ion itself (pKa = 3.37) reacts with hypochlorous acid; a reaction of N_2O_4 with DMA is hypothesized to form NDMA (Eqn. 2.16) (Choi and Valentine, 2003):

$$HOCl \;+\; NO_2^- \;\Leftrightarrow\; NO_2Cl \;+\; OH^- \qquad\qquad Eqn.2.14$$

$$NO_2Cl \;+\; NO_2^- \;\Leftrightarrow\; N_2O_4 \;+\; Cl^- \qquad\qquad Eqn.2.15$$

$$DMA \;+\; N_2O_4 \;\rightarrow\; NDMA \qquad\qquad Eqn.2.16$$
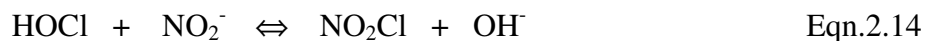
During this process, nitryl chloride hydrolyzes into nitrate as showed in reaction 2.11 (Margerum et al., 1978, 1994). This makes the situation very complex: N_2O_4 is formed in series reactions while HOCl and NO_2Cl compete for nitrite in parallel (Eqn. 2.14 and Eqn. 2.15); Furthermore, N_2O_4 formation (Eqn. 2.15) competes with nitryl chloride hydrolyzation (Eqn. 2.17) for nitryl chloride. Obviously, the presence of excess nitrite will favor N_2O_4 formation.

$$NO_2Cl+ \;OH^- \;\rightarrow\; NO_3^- \;+\; H^+ +\; Cl^- \qquad\qquad Eqn.2.17$$
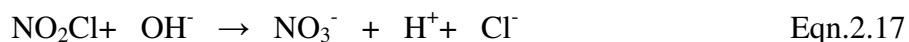
N_2O_4 exists in tautomerism forms: $ON\text{-}NO_3$, a very effective nitrosating agent, and $O_2N\text{-}NO_2$, a very effective nitrating agent (Challis and Hyrtopoulos, 1979). N_2O_4 undergoes rapid hydrolysis to NO_2^- and NO_3^- but the rate is slower than the nitrasation rate of most amines (Challis and Hyrtopoulos, 1979).

The schematic of the classical nitrosation and proposed free-chlorine-enhanced nitrosation mechanism presented in Figure 2.2 was developed by Choi and Valentine (2003).
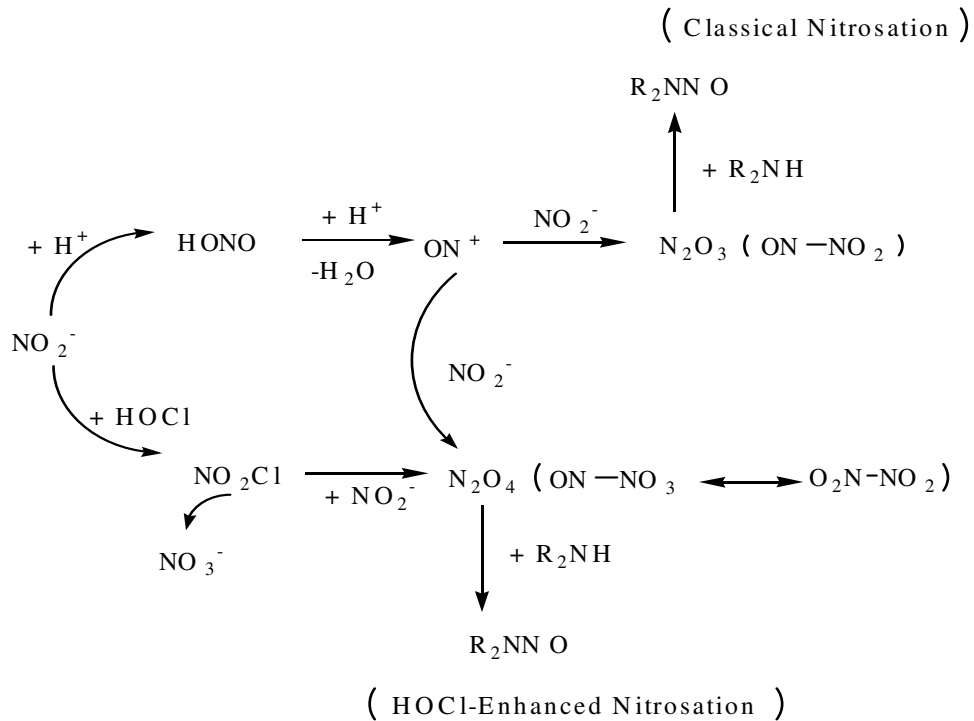
Figure 2.2. Schematic of classical nitrosation pathway and proposed free-chlorine-enhanced

nitrosation (Choi and Valentine, 2003)

2.3.5.3   *Unsymmetrical dimethylhydrazine (UDMH) oxidation*

NDMA formation during water and wastewater treatment involving chlorination is

also related to the formation and oxidation of 1,1-dimethylhydrazine, which is also known as

unsymmetrical dimethylhydrazine (UDMH). NDMA has been observed as a byproduct of

UDMH oxidation by cupric ion (Banerjee et al., 1984), potassium permanganate, iodate

(Castegnaro et al., 1986), hydrogen peroxide, and oxygen (Lunn et al., 1991; Lunn and

Sanone, 1994).

Because NDMA is formed when UDMH is oxidized, any chlorination reactions that

produce UDMH also should produce NDMA. It has been known for some time that UDMH

forms from the reaction between monochloramine and dimethylamine (Yagil and Anbar, 1962) and 1,1,1-trimethyl hydrazinium salt from the reaction of monochloramine with trimethylamine (Omietanski and Sisler, 1956). The kinetics of the formation of UDMH from the reaction between monochloramine and dimethylamine and the subsequent oxidation of UDMH at high concentrations of reactants were also investigated (Delalu et al., 1981; Delalu and Marchand, 1987, 1989a, 1989b). However, there are no reports on the investigation of NDMA formation via UDMH oxidation under the conditions encountered during water and wastewater treatment.

Reaction schemes for UDMH formation from monochloramine and dimethylamine at pH values greater than 10 via the Raschig Process (Clark, 1953) and the oxidation of UDMH to a variety of products in the presence of an oxidant at moderate pH levels were proposed by Mitch and Sedlak (2002) in Figure 2.3 and Figure 2.4.

The rate of UDMH formation is slow and increases with pH (Yagil and Anbar, 1962) while the UDMH oxidation occurs nearly instantaneously at circumneutral pH to form NDMA with low yields (<1%) (Mitch and Sedlak, 2002a). The formation of NDMA from oxidation of UDMH is maximized at neutral and high pH (Lunn et al., 1991). Furthermore, Mitch and Sedlak (2002a) observed that in the absence of ammonia, hypochlorite can also produce
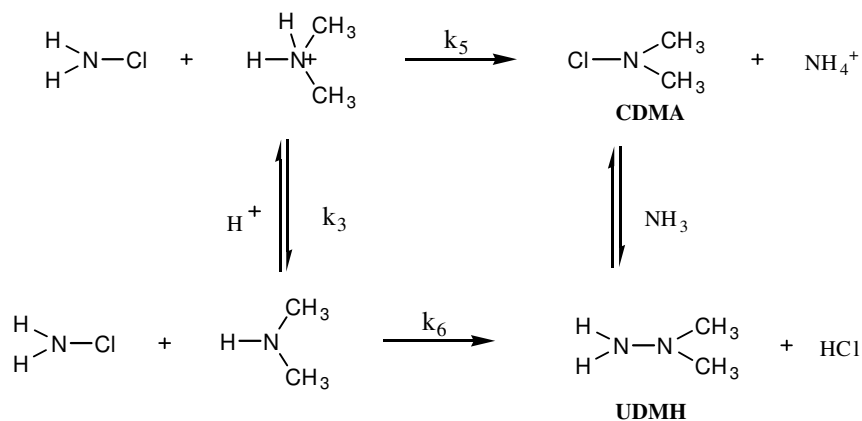
Figure 2.3. Proposed reaction scheme for NDMA formation via the UDMH pathway:

UDMH formation (Mitch and Sedlak, 2002) .
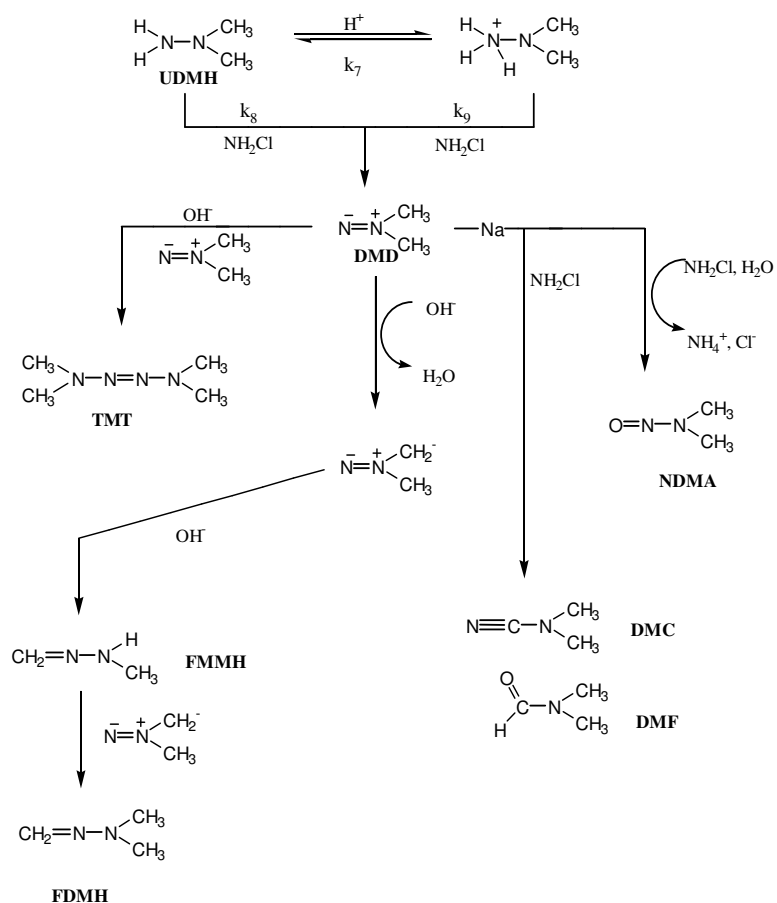
Figure 2.4. Proposed reaction scheme for NDMA formation via the UDMH pathway:

UDMH oxidation (Mitch and Sedlak, 2002) .

NDMA through reaction with secondary amines, but the formation rate was approximately

an order of magnitude lower than that with monochloramine.

Choi and Valentine (2002a and 2002b) proposed similar mechanisms for the NDMA

formation via UDMH pathway and presented rate constants for each reaction in the process

(Table 2.2).

Table 2.2. Proposed mechanism of NDMA formation mechanism via UDMH pathway
(Choi and Valentine, 2002b).

Reaction	Rate Constant (pH 7, 25 °C)	Reference
(1) $HOCl + NH_3 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} NH_2Cl + H_2O$	$k_1 = 4.2 \times 10^6 \text{ M}^{-1}\text{s}^{-1}$	Morris and Isaac, 1981
	$k_{-1} = 2.1 \times 10^{-5} \text{ M}^{-1}\text{s}^{-1}$	Morris and Isaac, 1981
(2) $HOCl + (CH_3)_2NH \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} (CH_3)_2NCl + H_2O$	$k_2 = 4.22 \times 10^4 \text{ M}^{-1}\text{s}^{-1}$	Choi and Valentine, 2002b
	$k_{-2} = 1.60 \times 10^{-6} \text{ M}^{-1}\text{s}^{-1}$	Yoon and Jensen, 1993
(3) $NH_2Cl + (CH_3)_2NH \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} (CH_3)_2NCl + NH_3$	$k_3 = 1.40 \times 10^{-1} \text{ M}^{-1}\text{s}^{-1}$	Isaac and Morris, 1983
	$k_{-3} = 5.83 \times 10^{-3} \text{ M}^{-1}\text{s}^{-1}$	Yoon and Jensen, 1993
(4) $NH_2Cl + (CH_3)_2NH \overset{k_4}{\rightarrow} (CH_3)_2NNH_2 + H^+ + Cl^-$	$k_4 = 1.56 \times 10^{-3} \text{ M}^{-1}\text{s}^{-1}$	Choi and Valentine, 2002b
(5) $(CH_3)_2NNH_2 + 2 NH_2Cl + H_2O \overset{k_5}{\rightarrow}$ $(CH_3)_2NNO + 2 NH_3 + 2 H^+ + 2Cl^-$	$k_5 = 2.38 \times 10^{-1} \text{ M}^{-1}\text{s}^{-1}$	Choi and Valentine, 2002b

The UDMH oxidation mechanism is consistent with observations of several investigators (Najm and Trussell, 2001; Berger et al., 2002; Najm and Ma, 2002; Wilczek et al., 2002). The use of monochloramine in water treatment greatly increases NDMA formation.

The slow rate of UDMH formation makes the overall reaction rate extremely low. This may cause an increasing NDMA formation problem in a distribution system when monochloramine is used to maintain a relatively stable chlorine residual.

2.3.5.4   NDMA Precursors

Each NDMA formation mechanism involves two types of NDMA precursors: inorganic nitrogen-containing species and organic nitrogen species.

Dimethylamine (DMA) has been determined to be the most effective organic nitrogen precursor of NDMA formation by both the nitrosation mechanism (Fiddler et al., 1972) and the UDMH oxidization mechanism (Mitch and Sedlak, 2002a). DMA is ubiquitously found in urine at an average concentration of about 40 mg/L (Brooks et al., 1972; Tricker et al., 1994), feces of dairy cattle and human beings at an average concentration of about 0.41 µg/mL (Van Rheenen, 1962; Tricker et al., 1994), higher plants (Smith, 1971), and algae (Rolle et al. 1971).

The tertiary amines containing dimethylamine functional groups such as trimethylamine, a compound that occurs in plants (Cromwell and Richardson, 1966), fish (Sasajima, 1968), and algae (Sakevich, 1970), are also possible NDMA precursors because DMA may be formed by demethylation of TMA. The formation of DMA as a result of TMA dealkylation has its greatest yield at pH 4.0 (Ayanaba and Alexander, 1974). However, DMA

accumulates slowly at these acid conditions and thus the NDMA formation from these tertiary amines has a low level of yields. It has also been demonstrated that nitrate containing sewage yielded more DMA than samples amended with nitrite.

DMA can also be formed from other industrial products containing dimethylamine functional groups including fungicides such as the pesticide tetramethylthiuram disulfide (thiram) (IARC, 1978; Maeda and Tonomura, 1971), pesticides, and herbicides (Fine, 1978; Child et al., 1996), drugs such as ranitidine (IARC, 1978), and amine-containing accelerators for vulcanization of tires. It was reported that addition of relatively high concentrations of trimethylamine or thiram to lake water or municipal sewage resulted in the microbiological production and eventual consumption of dimethylamine (Ayanaba and Alexander, 1974).

DMA concentrations in primary wastewater effluent range from 20 to 80 µg/L and those in secondary wastewater effluent are generally low with an average of 4 µg/L due to the degradation by bacteria (Mitch and Sedlak, 2002c; Mitch et al., 2003). Furthermore, the same scientists found that only 10% of NDMA formed during secondary wastewater effluent chloramination was contributed by dimethylamine (Mitch and Sedlak, 2002c; Mitch et al., 2003). A similar situation was found in natural waters where the yield of NDMA from chloramination of DMA was approximately 0.6% while the DMA concentrations were always below the detection limit of 4 nM (Gerecke and Sedlak, 2003).

Investigations on other organic nitrogen-containing molecules involved in the nitrosation of trimethylamine-N-oxide (Fiddler et al., 1972), a common constituent of urine (Zuppi et al., 1997) and may be broken down to trimethylamine by bacteria (Ohshima and Kawabata, 1978). The nitrosation of other quaternary amines that contained trimethylamine functional groups (Fiddler et al., 1972), the chloramination of primary amine

monomethylamine and the quaternary amine tetramethylamine, and amino acids or proteins

(Mitch and Sedlak, 2002b) were also studied. The results came out that either much lower

NDMA yield than with trimethylamine, or not much significant NDMA yields.

The most common inorganic nitrogen-containing species include nitrous anhydride

(N_2O_3) and dinitrogen tetroxide (N_2O_4), which act as active nitrosating agents in the classical

nitrosation and free-chlorine-enhance nitrosation, respectively, as discussed above. Nitrite,

the origin of these active agents and the inorganic precursor of the nitroso group of NDMA,

may accumulate during the reduction of nitrate or the oxidation of ammonium under alkaline

conditions (Stojanovic, 1958). Monochloramine is another common inorganic nitrogen-

containing species during NDMA formation when ammonium is present and it's very

important in the UDMH oxidation mechanism.

2.3.5.5   Role of Natural Organic Matter in NDMA formation in natural waters

Natural organic matter (NOM) is an assemblage of organic compounds derived

mainly from the leaching of dead vegetation and animal material and is found in practically

every terrestrial environment. NOM in and of itself is nonhazardous, however, it consists of

complex mixtures of organic compounds with relatively unknown structures and chemical

composition. These compounds are responsible for the formation of halogenated disinfection

by-products (DBPs) during water treatment. These DBPs may cause health problems due to

their carcinogenicity and toxicity (Stevens et al. 1976; Christman et al. 1983; Gang et al.,

2003). NOM is generally measured as total organic carbon (TOC) or dissolved organic

carbon (DOC). The TOC concentrations in most surface waters and groundwaters are in the

low mg/L range, usually below 10 mg/L.

33

Many studies on the nature of DOC in natural waters have been conducted to investigate the inherent chemical complexity of the organic carbon. Thurman and Malcolm (1981) developed a procedure utilizing XAD-8 resin followed by size-exclusion chromatography, hydrogen saturation by ion exchange, and lypholization to obtain aqueous humic substances. The same authors improved their method by using a two column array of XAD-8 and XAD-4 resins in series resulting in the hydrophobic acids being retained on the XAD-8 resin, the hydrophilic acids being retained on the XAD-4 resin, and the hydrophilic neutral and basic fraction remaining in the water samples (Aiken et al., 1992). It was also found that for samples from diverse environments, between 23 and 58% of DOC was composed of hydrophobic acids that are mainly aquatic fulvic acid, while 7 to 25% of DOC was hydrophilic acids. A comprehensive approach to isolating and fractionating the DOC from natural water was also put forward by Leenheer (1981). A series of resin adsorbents including Amberlite XAD-8 resin, a strong acid Bio-Rad AG-MP-50 cation-Exchange Resin, and a weak base Duolite A-7 Anion-Exchange Resin, were applied to isolate complex mixtures of organic solutes from water and fractionate these solutes into six compound categories: hydrophobic base, hydrophobic acid, hydrophobic neutral, hydrophilic base, hydrophilic acid, and hydrophilic neutral. The analysis by infrared spectra showed several distinguishing features indicating a relatively distinct and meaningful DOC fractionation were: the hydrophobic acids were similar to fulvic acid; the hydrophobic neutral appeared to be a mixture of hydrocarbons and carbonyl compounds; the hydrophilic bases were most likely amphoteric proteinaceou; the hdrophilic acid seemed like a mixture of hydroxyl acids; the hydrophilic neutral were mostly polysaccharide. Recoveries of 95% and 115% of DOC

from the adsorbents for an oil-shale retort wastewater and river water were obtained from the resin adsorbents.

Based on the study on fractionation of DOC in waters, natural organic matter in natural waters can be operationally classified by abundance into six major groups: humic substances including fulvic and humic acids, hydrophilic acids which is also called hydrophilic humic substances, carboxylic acids, amino acids, carbohydrates, and hydrocarbons (Thurman, 1985, 1986). A histogram of dissolved organic carbon in Figure 2.5 displays the relative abundance of these organic compounds in different natural waters (Thurman, 1986). For most natural waters, approximately 30-50% of the DOC is aquatic fulvic and humic acids and makes the humic substances dominant group of natural organic compounds in natural water, 30% of the DOC is hydrophilic acids, and the identifiable compounds including carboxylic acids, amino acids, carbohydrates, and hydrocarbons accounts for the remaining 20% of the DOC.

The fractionation techniques were then widely applied in the study on the reactivity of NOM with free chlorine or monochloramine to form halogenated DBPs. The influence of structural characteristics of NOM on disinfection by-product formation was investigated and results showed that hydrophobicity and alkalinity of the fraction of DOC in water (Stevens, et al. 1976; Christman, et al. 1983; Croue et al., 2000; Rostad et al., 2000; Gang, et al., 2003; Wu et al., 2003). A recent study on NDMA formation found a weak correlation observed between the NDMA precursors and the DOC contents and indicated that NDMA formation appeared to be related to DOC (Gerecke and Sedlak, 2003). The chloramination of isolated natural organic matter accounts for a significant fraction of the precursors. This gives a clue

that it is reasonable to hypothesize that structurally complex NOM could have some relation

to the formation of another disinfection by-product, NDMA.
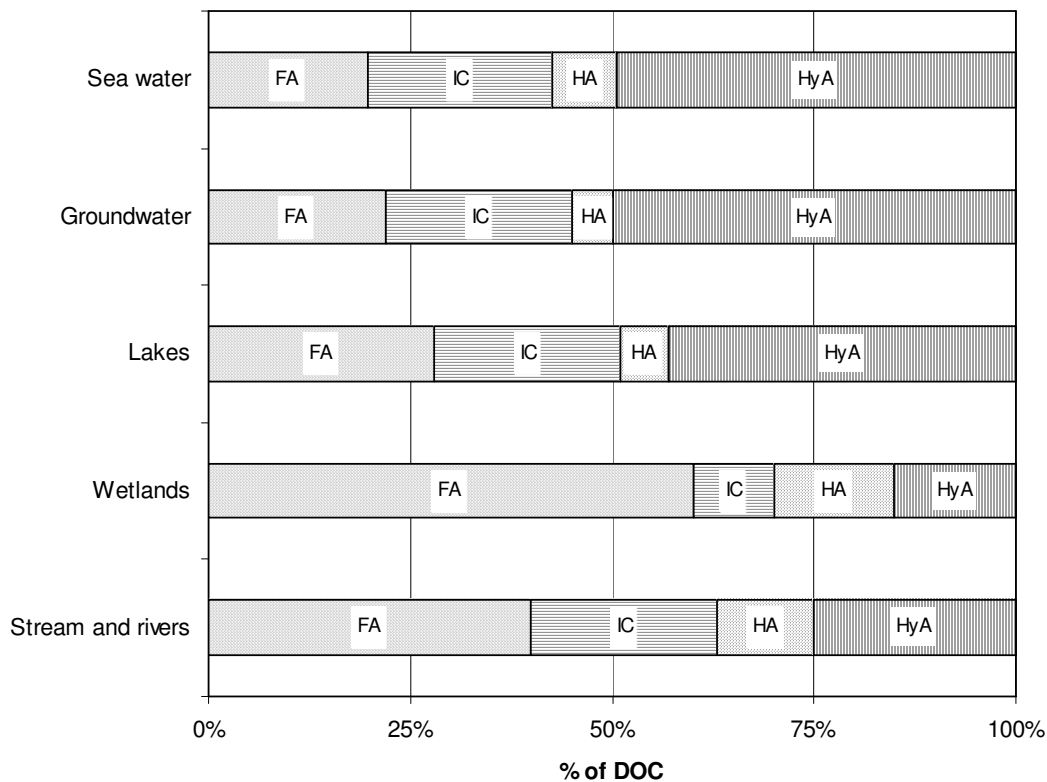
FA: Fulvic acid   IC: Identifiable compounds;

HA: Humic acid   HyA: Hydrophilic acids.

Figure 2.5. Distribution of dissolved organic compounds in natural waters. (Thurman, 1986).

2.3.5.6   Role of Bromide Ion in NDMA formation

Bromide ion is frequently a trace component of drinking water and wastewater. It is

easily oxidized by free chlorine so it competes with ammonia present in water for free

chlorine to form hypobromous acid (HOBr) (Bousher et al., 1986). It also can be oxidized by

monochloramine to form bromamines just like chloramines although the rate of reaction is much slower than the oxidation by free chlorine (Trofe et al., 1980). Depending on the pH and salinity, either monochloramine or bromamines may predominate (Johnson and Inman, 1977). Compared to monochloramine, the bromamines are less persistent in water system (Mills, 1979; Bongers et al., 1977). Given the similarity of bromamine to chloramine chemistry and the generally increased reactivity of bromamines compared to chloramines, it is expected that bromamines react with amines in a manner analogous to monochloramine to form NDMA (Mitch et al., 2003). The increased negative charge of the brominated nitrogen of monobromamine increased the rate of NDMA formation by UDMH pathway. Catalysis of nitrosation of NDMA precursors by halide ions such as bromide and chloride has been reported (Douglass et al., 1978).

2.4   Summary

NDMA, a disinfection by-product of monochloramine, has aroused concern since it has been observed in drinking water and groundwater at levels up to 3 µg/L. The Ontario Ministry of the Environment has set Maximum Acceptable Concentration of 9 ng/L for NDMA and the state of California has established an action level of 10 ng/L for NDMA.

NDMA could be analyzed by extraction methods and GC/MS analysis. GC/MS/MS and GC/HRMS usually could achieve the goal of trace level of NDMA in water. NDMA formation mechanisms usually include nitrosation and UDMH oxidation pathways and the most effective precursors of NDMA is dimethylamine. Natural organic matter is an assemblage of organic compounds with complex structures and chemical compositions and responsible for halogenated disinfection by-products (DBPs) during water treatment. The

isolated techniques on NOM provide possibility to further study on NDMA. Bromide ion is a trace component of drinking water and wastewater and its reactivity with chlorine and monochloramine make it affect NDMA formation.

In this study, analytical methods for NDMA based on two extraction methods and GC/MS at trace level in water will be developed to avoid investment on expensive instrument. The NDMA concentrations in drinking water utilities using chloramine as primary disinfectants in Missouri will be determined. The NDMA formation study related with NOM in natural waters will be investigated and role of bromide ion in the formation process will also be addressed.

CHAPTER 3

METHODS, PROCEDURES AND FACILITIES

3.1   Chemicals, Reagents and Materials

Chemicals were obtained from the following sources at the specified purities:

NDMA stock solutions, 100.4 µg/mL in methanol, were used as standard without

purification and purchased from Ultra Scientific Company; 250 Smith Street, North

Kingstown, RI.

NDMA-d6, 98%, 1 mg/mL in methylene chloride-d2, was used as a surrogate and

internal standard and purchased from Cambridge Isotope Laboratories; 50 Frontage Road,

Andover, MA. NDMA and NDMA-d6 were diluted with methylene chloride to make

reference standard solutions and for recovery studies.

Ambersorb 572® with mesh 20-50 was manufactured by Rohm and Haas Company

and purchased from Supelco/Sigma-Aldrich Chemical Company; Ambersorb 348F® with

mesh 50-100 was manufactured by Rohm and Haas Company purchased from Sigma-Aldrich

Chemical Company.

Amberlite XAD-8 resin as an industrial grade preparation with apparent density of

39.4 lbs/ft^3 and uniformity coefficient of 1.94 was manufactured by Rohm and Haas

Company and purchased from Supelco Company; 595 North Harrison Road, Belleforte, PA.

Amberlite XAD-4 resin as an industrial grade preparation with uniformity coefficient of 1.57

was obtained from the same manufacturer as Amberlite XAD-8 resin.

The following chemicals were obtained as certified A.C.S. grade or better from Fisher

Scientific Company: Sodium hypochlorite (4-6%) (NaOCl) at purified grade, ammonium

chloride (NH_4Cl), sodium bicarbonate powder ($NaHCO_3$), sodium thiosulfate crystal (NaS_2O_3), disodium Ethylenediamine Tetraacetate (EDTA), potassium Iodide (KI), hydrochloric acid (HCl), sodium hydroxide (NaOH), anhydrous sodium phosphate (Na_3PO_4), sulfuric acid (H_2SO_4), sodium chloride (NaCl) at USP/FCC grade, potassium bromide (KBr) granular purified, methanol (CH_3OH) at optima grade, methylene chloride (CH_2Cl_2) at HPLC grade, and DIUF water used as chlorine-free water and NDMA-free water.

The following chemicals were from Sigma-Aldrich Company: Ammonium Iron (II) sulfate hexahydrate ($Fe(NH_4)_2(SO_4)_2$ $6H_2O$, crystalline) as A.C.S. reagent, potassium Phosphate Monobasic Anhydrous (KH_2PO_4) as A.C.S. reagent, and potassium Phospahte dibasic anhydrous (K_2HPO_4) as A.C.S. reagent; L-ascorbic acid; N,N-Diethyl-p-Phenylene-Diamine Sulfate Salt (DPD). The air and nitrogen compressed gas tank was provided by the University of Missouri-Columbia.

Glass filtration apparatus, 2L separatory funnels, were Corning PyrexPlus squibb separatory funnels with PTFE stopcock plug and standard taper stopper are purchased from Fisher Scientific. Rotary evaporator was Rotavapor Evaporation Systems Model RE-46 obtained from Fisher Scientific.

Masterflex peristaltic pumps was obtained from Cole-Parmer Instrument Company and used to backflush the resin during fractionation process. The pH meter was from Fisher Scientific and used for sampling, controlling pH during the fractionation process, and monitoring formation process.

3.2   Preparation for the solutions

Water samples for the determination of NDMA occurrences in drinking water utilities and water samples for the NDMA formation studies were pretreated before analysis and reactions. Monochloramine solutions were prepared in lab before application. The methods are introduced in this section.

3.2.1   Water sample collection and preparation

Finished water samples were collected from 10 drinking water utilities in Missouri to investigate the relationship between DOC contents in natural waters and NDMA levels in finished drinking waters. All water utilities used monochloramine as a disinfectant. It was produced by adding gas or liquid chlorine to the water followed by the addition of gas or liquid ammonia, ammonium sulfate, or by utilizing the existing ammonium in the influent raw water (Table 3.1). All water samples were collected in 4-L pre-cleaned amber bottles which were prepared using the following procedures: rinsing with acetone, hexane, distilled water and heating to 105 °C in the oven overnight by the standard method (Clesceri et al., 1998) and then adding with ascorbic acid at 40 mg/L or excess level and storing at 4 °C in the refrigerator.

Seven raw surface water samples were collected in the 4-L pre-cleaned amber bottles (prepared as before) at the water inlet of utilities for the NDMA formation potential test. Water samples were filtered with prefilter glass fiber paper and 0.45 µm glass fiber filter paper. About 40 mL of each filtered raw water samples were acidified to pH 2 with phosphoric acid and stored at 4 °C for DOC analyses while all other raw water samples were stored at 4 °C for future use (Eaton, et al. 1998).

Table 3.1. Chemicals and dosage added to finished water samples by utilities

No.	Location	Chemical added to provide N	Dose	Chemical added to provide Cl	Dose	Residual chloramine (ppm)	Residual chloramine (mM)
1	Independence	ammonium gas	0.4 ppm	Cl_2 liquid	2.5 ppm	2	0.0388
2	Kirkwood	Granular ammonium sulfate	15lb/2.6 mgd	Cl_2 gas	120-150 lb/2.6 mgd	3	0.0582
3	Clanrance Cannon	ammonium gas	*	Cl_2 gas	*	2.5-3.0	0.0485-0.0582
4	Tri-County	Ammonium exist in raw water	1.7 ppm	Cl_2 gas	10.4 ppm	2.4-2.8	0.0466-0.0543
5	Kansas City	liquid ammonium		Cl_2 gas	7 lb/mgd	2-2.2	0.0388-0.0427
6	Jefferson County	Granular ammonium sulfate	40lb/1.5 mgd	Cl_2 gas	100 lb/1.5 mgd, or 50 lb/1.1mgd	2.5	0.0485
7	Howard Bend	liquid ammonium	8-18 lb/mgd	Cl_2 gas	20lb/mgd	2.5	0.0485
8	Jefferson City	Granular ammonium sulfate	0.7 ppm	liquid Cl_2 12.5%	30-35 lb/mgd	2.4	0.0466
9	Chain of Rocks	Aqueous ammonium 19%	10-20 lb/mgd	Cl_2 gas	25 lb/mgd	2.5	0.0485
10	Sedalia	liquid ammonium	1.5 ppm	Cl_2 gas	100 lb/3mgd	2.3-2.4	0.0446-0.0466

* No weight of chlorine or ammonium available; Cl/N = 4.

3.2.2 *Preparation of monochloramine*

Monochloramine was prepared freshly because of its ability to autodecompose at high concentrations (Jafvert and Valentine, 1992). Preparation for 100 mM monochloramine was done by dissolving a calculated amount of ammonium chloride in 4 mM sodium bicarbonate buffer solution and chilled to 5 °C. Sodium hypochlorite (4-6%) concentration was measured for its exact concentration level before being used every time and was then added slowly to a rapidly stirred ammonium chloride buffer solution at a molar ratio of 1:1.2 (hypochlorite to ammonia). The mixed solution was stored at 4 °C for one hour before use and discarded after 2 hours.

3.3 Analytical methods

NDMA analysis methods in water on both LLE and SPE methods are described in this section. Monochloramine concentration was analyzed before application. NDMA analytical method is introduced together with DOC analytical method.

3.3.1 *NDMA analytical method*

NDMA of the water samples were analyzed by extraction and followed by GC/MS/SIS analysis as mentioned in the experimental section. The involved extraction methods include liquid-liquid extraction and solid phase extraction. The procedures for the extraction methods and instrumentation conditions are described below.

3.3.1.1 Solid Phase Extraction

A 500 mL water sample was placed in a 1 L amber bottle with Teflon-lined cap. Twenty-five µL of 1mg/L standard NDMA-d6 was added into the water sample as an internal standard. 125 mg Ambersorb 572, that was previously baked at 300 °C in a muffle furnace for 1 hour, was added to the sample to adsorb NDMA in the water sample, and the sample was shaken for an hour on a rotary shaker at a speed of 250 rpm. No.4 Whatman filter paper was used to filter the adsorbent. The adsorbed Ambersorb 572 beads were allowed to air dry in the hood for 1 hour. Then, the dried Ambersorb 572 was wrapped in a filter paper and carefully transferred to a 2 mL autosampler vial and 500 µL of methylene chloride was added to desorb the NDMA from the Ambersorb. Finally, 8 µL of final extract was injected into the GC/MS for the analysis.

3.3.1.2 Liquid-liquid Extraction

One-liter water sample was transferred to a two-liter separatory funnel and 50 µL of 1mg/L NDMA-d6 was added as an internal standard and then 100 g NaCl was added to increase the extraction efficiency. 60-ml methylene chloride was added to the separatory funnel and the sample was extracted by vigorously shaking the funnel for 2 minutes. The organic layer was allowed to separate from the water phase for 20 minutes. The methylene chloride extract was collected in a 500-ml Erlenmeyer flask containing approximately 7 grams of anhydrous sodium sulfate. Second and third extractions were performed in the same manner and the extracts were combined together. The flask was allowed to sit overnight to ensure no water in the extracts. Combined extract was transferred into a concentrate flask and the Erlenmeyer flask was rinsed with 2-25 ml of methylene chloride. The extract was

concentrated using a Rotovapor first to about 10 mL and then using nitrogen gas to about 1 ml at 35°C in a water bath. The extract was transferred into an autosampler vial and reconstituted to 1.0 mL with methylene chloride and analyzed by GC/MS.

3.3.1.3   Instrumentation conditions

The analysis of NDMA was carried out using Varian CP-3800 gas chromatograph coupled to a Saturn 2000 MS with ion trap detector. Extracts were analyzed by low-resolution GC/MS with positive chemical ionization using reagent gas of methanol in the mode of Selected Ion Storage (SIS). SIS mode is an operation of the mass spectrometer in which the intensities of some specific ion beams are recorded rather than the entire mass spectrum and thus help to increase the detection limit and provide positive identification of NDMA. NDMA-d6 was used as an internal standard to monitor the procedure efficiency and also to ensure the uniform injection of autosampler. The system was equipped with a 60 m, 0.32 mm ID, 1.8-micron film thickness, J&W Scientific DB-VRX column. The conditions of the system are described as below:

Autosampler

8200CX making 8.0 µl injections, 0.2 µl per second injection speed, sandwich injection technique.

Gas Chromatograph

Column Flow: 1.2 ml/min;

1079 Injector Program: 37 °C for 0.8 min, ramp to 200 °C @100 °C per min. Split 5:1 for 0.8 min. Splitless until 2.0 min, then split at 100:1;

Column Temperature Program: 35 °C hold 4.0 min, ramp to 140°C@20°C/min. no hold time and then ramp to 200°C@50°C/min. hold for 5.0 min.

Mass Spectrometer

Ion Trap Temperature: 150°C;

Manifold 40°C;

Emission Current: 50 µA;

Multiplier offset: 200V;

Scan Time: 0.43 sec;

Acquisition Segment: Scan Range: 72-84 m/z Methanol CI;

CI storage level: 19 m/z;

Ejection amplitude: 15 V;

Background mass: 55 m/z;

Max Ion time: 2000 usec;

Max reaction time: 40 msec;

Target TIC: 10000 counts;

Prescan Ion time: 200 µsec;

MRM two ions: (75 m/z NDMA) Isolation Time: 5 msec;

Isolation Window: 3 m/z;

(81m/z NDMA-d6) Isolation Time: 5 msec;

Isolation Window: 3 m/z

3.3.2   Monochloramine analytical method

The concentration of monochloramine was measured by using N, N-diethyl-p-phenylenediamine ferrous ammonium sulfate (DPD-FAS) method from EPA standard method (Clesceri, et al. 1998).

Phosphate buffer solution was prepared by dissolving 24 gram anhydrous Na_2HPO_4 and 46 g anhydrous KH_2PO_4 in distilled water and then combining with 100 mL distilled water in which 800 mg disodium ethylenediamine tetraacetate dihydrate (EDTA) had been dissolved. The solution was diluted to 1 L with distilled water.

N,N-Diethyl-p-phenylenediamine (DPD) indicator solution was obtained by dissolving 1.1 g anhydrous DPD sulfate in chlorine-free distilled water containing 8 mL H_2SO_4 (1:3 for $H_2SO_4:H_2O$) and 200 mg disodium EDTA and diluted to 1 L, stored in a brown glass-stoppered bottle in the dark, and discarded after 1 week.

Standard ferrous ammonium sulfate (FAS) titrant was prepared by dissolving 1.106 g $Fe(NH_4)_2(SO_4)_26H_2O$ in distilled water containing 1 mL H_2SO_4 (1:3 for $H_2SO_4:H_2O$) and diluted to 1 L with freshly boiled and cooled distilled water. This standard was used for 1 month, and the titer checked by potassium dichromate.

Potassium iodide solution was obtained by dissolving 500 mg KI and dilute to 100 mL, using freshly boiled and cooled distilled water. The solution was stored in a brown glass-stoppered bottle in a refrigerator. It was discarded when solution became yellow.

Since this method is valid for concentrations of total chlorine up to 5 mg/L, it was necessary to use a smaller sample and dilute it to a total volume of 100 mL when the total chlorine exceeded 5 mg/L in the water sample. 5 mL of buffer reagent and DPD indicator solution was placed in titration flask and 100 mL of water samples was added and mixed

47

(Buffer solutions and DPD indicators must be added first, otherwise test does not work). Solution was titrated rapidly with standard standard FAS titrant until red color is discharged (Reading A). Two drops (0.1 mL) KI solution or one small crystal of KI (about 0.5 mg) was added and mixed. The solution would turn red again with monochloramine present. Titrating was continued until red color was discharged again (Reading B). Reading A is the value of free chlorine in the solution and reading (B-A) is the concentration of monochloramine in tested water sample. And for a 100-mL sample, 1.00 mL standard FAS titrant equals 1.00 mg Cl as Cl_2/L.

3.3.3   DOC analysis

Water samples was prefiltered and filtered with 0.45 μm glass fiber filter paper from each site. They were collected in 40-mL glass vials which were previously baked at 105 °C. Phosphate acid was added to adjust pH to be 2.0 and the vials were sealed with Teflon screw-on caps. Samples were stored in the refrigerator at 4 °C until analysis. Samples of column effluents from XAD-8 and XAD-4 resins were also collected and stored in the same manner. The DOC analysis was conducted on Phoenix 8000 UV-Persulfate TOC Analyzer using the EPA persulfate standard method (Clesceri, et al. 1998). Sample standards were run after each ten samples. The carbon analyzer was standardized for a DOC range from 0.1 mg C/L to 10 mg C/L. Sample accuracy was ±0.03 mg C/L using potassium biphthalate, $C_8H_5KO_4$, and fulvic acid standards. Sample precision (standard deviation) was ±0.02 mg C/L.

3.4   NDMA formation potential reaction

This experiment was conducted in 1-L brown amber bottles. All bottles were rinsed successively with acetate, hexane, distilled water, and heated at 105 °C for at least 2 hours. NDMA formation potential reactions were all conducted under room temperature (20 to 25 °C) and under dark conditions. Raw water samples were filtered with glass fiber prefilter paper and 0.45 µm glass fiber filter paper. Unless otherwise specified, 500 mL of filtered water samples were buffered at pH 7.0 (±0.5) with 10 mM phosphate buffer and dosed with 100 mM monochloramine stock solutions prepared fresh daily as described previously and standardized by iodometric titration. Reactions were quenched by addition of excess ascorbic acid.

To identify and control the total concentration of NDMA precursors, water samples were exposed to relatively high concentrations of monochloramine for sufficient period of time and the total concentration of NDMA that could be formed when disinfected with monochloramine (Mitch and Sedlak, 2003; Gerecke and Sedlak, 2003). This determined total concentration of NDMA was then used as a surrogate for all compounds that could form NDMA during the chloramination. This NDMA precursor test was similar to the trihalomethane formation potential (THMFP) test (Stevens and Symons, 1977), in which case, THMFP was the difference between the InstTHM concentration, which was the THM concentration measured from the zero time sample, and the TermTHM concentration, which was the THM concentration for the longest reaction time.

In the NDMA formation potential experiment, two levels of concentration of monochloramine were used: high concentration of 1 mM which was used to evaluate the formation potential of NDMA in natural water samples, and a comparable concentration of

0.1 mM as used under actual treatment conditions in water utilities which was used to compare to the NDMA results from the finished water from the utility. A 7 day experiment of water samples reacting with high concentration level of monochloramine (1 mM) showed that the NDMA concentration increased with the reaction time and after two days had little change. The final monochloramine residuals were similar between water samples. This indicated that there was no further demand and that the precursors in water samples had been completely consumed in the reaction. This concentration of monochloramine was used for the 2 days (48 hours) tests. The formed NDMA was used as a surrogate for NDMA precursors.

In the kinetics study of NDMA formation, the longest time for the study was set to be 7 days (168 hours), six other reaction periods were also tested. For the effect of pH on the NDMA formation study, pH values of 6, 7 and 9 were used to determine the effect of pH conditions on the NDMA formation.

3.5   Water sample fractionation

The isolation procedure used two types of Amberlite XAD resins in series in chromatography columns with reservoirs as shown in Figure 3.1: XAD-8 resin and XAD-4 resin which were macroporous methylmethacrylate copolymer with an average surface area of 450 m^2/g and 725 m^2/g, and an average pore diameter of 250 A and 40 A, respectively.
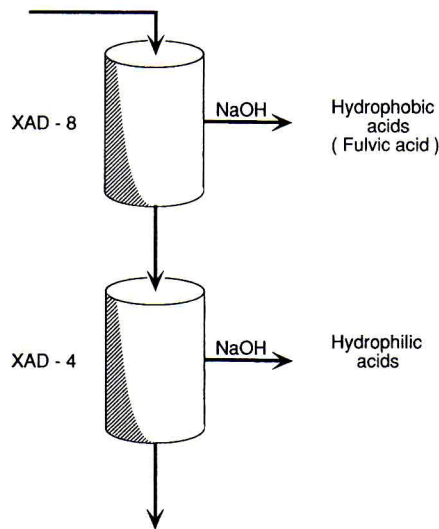
Hydrophilic fraction (hydrophilic bases and neutrals)

Figure 3.1. Schematic diagram of the XAD-8/XAD-4 isolation scheme. (Aiken et al., 1992)

3.5.1   Resin and column preparation

The Amberlite XAD resins were supplied in wet form. Since prolonged exposure to air during shipment or storage may cause the material to dry, they were wetted first when obtained from the supplier and before use. This was done by immerging the resin into sufficient methanol, stirring the resin to mix it completely, let it stand for 5-10 minutes, and then decanting most of the methanol. Next the distilled water was used and the same steps were following as previously described for method. The resins used in the isolation process were fully hydrated; the resin columns would not become dry during the preparation or subsequent use. Before the resin slurry was added to the column, deionized water was added to the empty column up to about 1" (2.5 cm) height. The water was slowly poured into the resin slurry in the column and excess water drained through the bottom of the column but liquid level was kept above the top of the resin slurry bed. Two bed volumes of deionized

51

water were passed through the resin bed to remove the remaining methanol in the resin at the rate of 1 ml/min.

3.5.2   Determination of the resin adsorbent quantities

Adsorption or elution of organic solutes on both resins caused the hydrophobic-hydrophilic separation of the DOC fractionation which is controlled by the polarity of the solute and by the ratio of the resin quantity to the volume of water passed through the resin bed. The hydrophobic-hydrophilic break was an operationally defined separation in which the crossover of hydrophilic fraction into the hydrophobic fraction was mathematically defined. For the DOC fractionation, hydrophobic solutes was defined as those solutes that were greater than 50% retained on XAD resins at a given ratio of resin to water passed through the column, and hydrophilic fraction was defined as those solutes that were greater than 50% eluted at the same ratio of resin to water (Leenheer, 1981).

The breakthrough curve of a hypothetical organic solute in the XAD-8 resin is illustrated in Figure 3.2 and the examination of the figure shows that the integrated area of solute adsorption equals to the integrated area of solute elution at 2 V_E. To design a DOC fractionation, the column distribution coefficient, hydrophobic-hydrophilic break $k'_{0.5r}$, of a hypothetical solute which is 50% retained and 50% eluted by the system and determined by Leenheer (1981) as follows.

The elution volume V_E of a solute from the resin column is determined by Eqn. 3.1.

$$V_E = V_0 \times (1 + k')$$
Eqn. 3.1

where $\qquad\qquad\qquad$ V_0= void volume

k'=(mass of solute sorbed on XAD resin)/

$\qquad\qquad\qquad\qquad$ (mass of solute dissolved in water) $\qquad$ Eqn. 3.2

V_E refers to the volume where effluent concentration of DOC is 50% of influent concentration while $V_{0.5r}$ is defined as the water volume passed through the resin column when 50% solute retention on the resin and 50% retention in the water.

$$V_{0.5r} = 2\, V_E$$
Eqn. 3.3

And

$$V_{0.5r} = 2V_0(1 + k'_{0.5r})$$
Eqn. 3.4

For a 1-L water sample, the DOC fractionation with hydrophobic-hydrophilic break is at $k'_{0.5r}$ =50, from the equation 3.4, resin void volume should be 9.8 mL. As the void volume of XAD-8 resin is ~65% of its bulk column volume, a 15 mL of the XAD-8 resin volume is required for this fractionation.
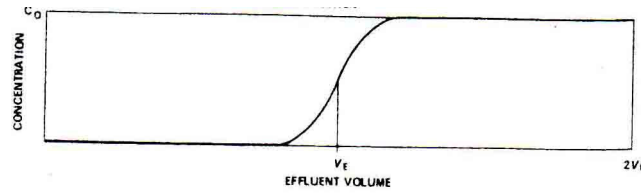
Explanation

C_0 = Influent concentration

V_E = Breakthrough (Elution) Volume (C = 0.5 C_0)

$2V_E$ = Effluent volume of 50% retention, 50% elution

Figure 3.2. Frontal chromatography breakthrough curve. (Leenheer, 1981)

3.5.3   Generation of dissolved organic carbon fractions

With the application of XAD-8 and XAD-4 resins, natural organic matter in water could be isolated into three different fractions. The detailed isolation and recovery procedures are described in the following sections.

3.5.3.1   Hydrophobic fraction

The filtered water sample was acidified to pH 2.0 by using sulfuric acid and allow to flow through the XAD-8 resin column from the top reservoir at a flow rate of 1 mL/min. Following the sample, two bed volumes of deionized water were applied to clean the water sample in the void of resins. The hydrophobic fraction, mainly fulvic acids, humic acids, and hydrophobic neutrals (Leenheer, 1981; Aiken et al., 1992; Malcolm and MacCarthy, 1992), was backflush eluted with 0.1 N NaCl using the peristaltic pump at the flow rate of no more

54

than 60 mL/min or less and diluted with deionized water to the volume of the water sample

flowed through the column. Samples were analyzed for DOC.

3.5.3.2   Transphilic fraction

The sample effluent from the XAD-8 resin column went through the XAD-4 resin

column at a flow rate of no more than 60 mL/min. Following the sample, two bed volumes of

deionized water were applied. The transphilic fraction, also called hydrophilic acids

(Leenheer, 1981; Leenheer and Noyes, 1984; Aiken et al., 1992; Malcolm and MacCarthy,

1992), was backflush eluted with 0.1 N NaCl with the peristaltic pump at the flow rate of less

than 60 mL/min and diluted with deionized water to the volume of the water sample flowed

through the column. Samples were analyzed for DOC analysis.

3.5.3.3   Hydrophilic fraction

The sample effluent from the XAD-4 resin column was the hydrophilic fraction, also

recognized as hydrophilic neutrals and bases (Leenheer, 1981; Leenheer and Noyes, 1984;

Aiken et al., 1992; Malcolm and MacCarthy, 1992). Samples were analyzed for the DOC and

the remaining samples were stored at glass bottles for the future application.

3.5.4   Resin cleaning, regeneration and storage

The used resins were cleaned with 0.1 N NaOH, methanol solvent, and deionized

water respectively. Cleaned XAD resins were stored in methanol.

CHAPTER 4

NDMA ANALYTICAL METHOD ASSESSMENT

4.1   Introduction

A Liquid-liquid extraction method and solid phase extraction method were both used in the experiment to obtain optimal analytical results on the detection of trace levels of NDMA in water samples. A general assessment of both methods is based on analytical results of NDMA in water samples described in this chapter.

4.2   Analytical results on non-extracted NDMA solution

NDMA solutions without extraction procedure were used to determine peak positions of chemicals and instrument detection limit to assure the proper working conditions of the instrument.

4.2.1   *NDMA peak and NDMA-d6 peak*

Stock solution of NDMA with a concentration of 100 mg/L (ppm) and stock solution of NDMA-d6 with a concentration of 1000 mg/L were used in the study. Under the instrument conditions, 1 mg/L of NDMA in methylene chloride and 1 mg/L of NDMA-d6 in methylene chloride were used to determine the peak location. Figure 4.1 illustrates a typical chromatogram and mass spectrum for a 50 µg/L (ppb) of NDMA lab fortified blank. The peaks for NDMA-d6 and NDMA are at approximately 11.89 and 11.92 minutes respectively.

The mass spectrums show masses for both the NDMA and NDMA-d6. Generally, for the same concentration, NDMA has higher peaks and larger peak area than NDMA-d6.

4.2.2   Instrument Detection Limit (IDL) for standard solution

Instrument Detection Limit (IDL) is the lowest limit that the instrument can detect and it reflects the accuracy of the instrument. It is determined on samples which have not gone through any sample preparation steps. Seven different solutions with the same spike concentration of 2 µg/L (ppb) of NDMA were used to determine the IDL of the standard solution without extraction. The data of the seven solutions IDL are listed in Table 4.1.
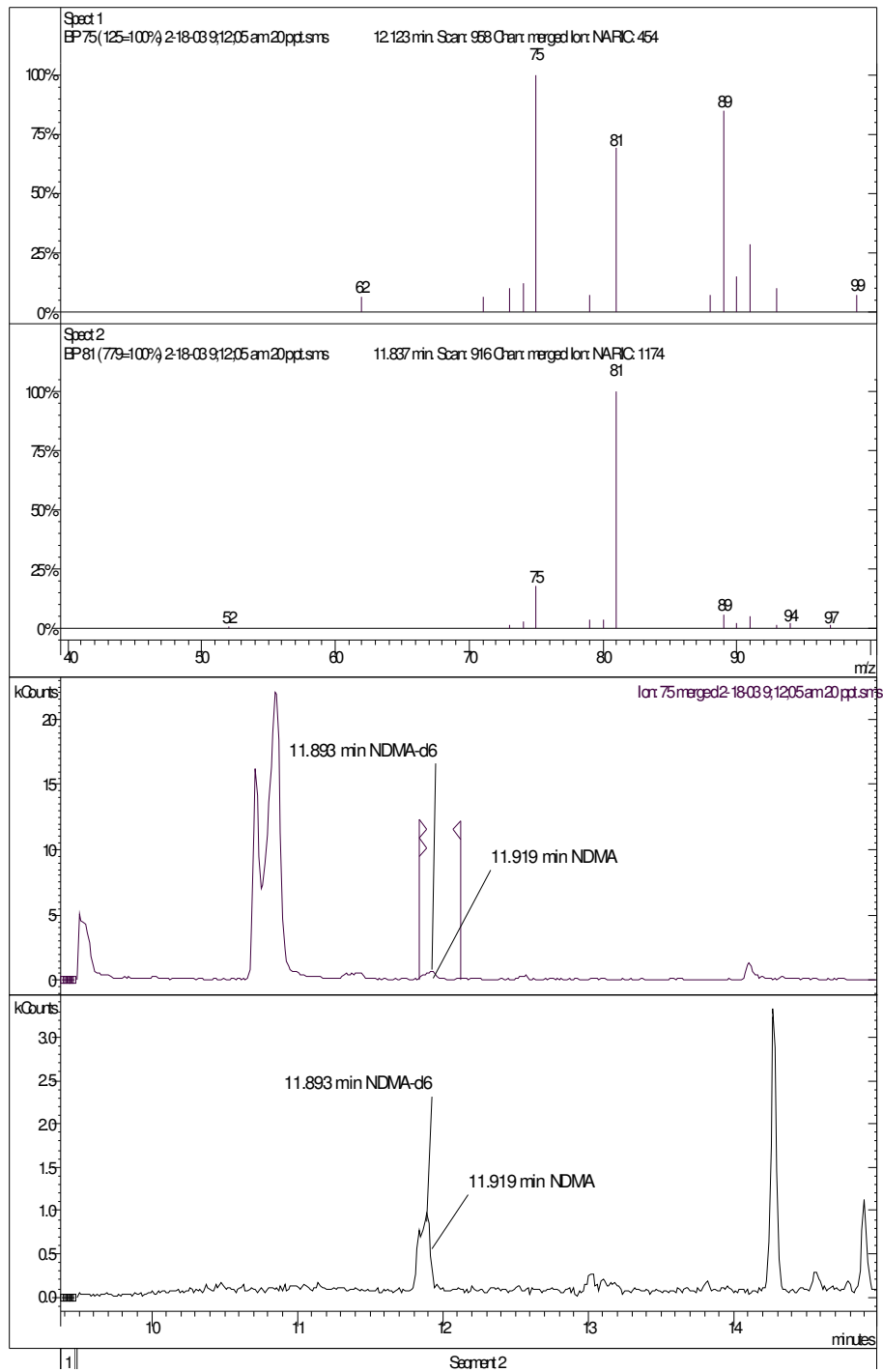
Figure 4.1. Chromatogram and mass spectrum for NDMA and NDMA-d6

58

Table 4.1. Analysis data for Instrument Detection Limit (IDL) determination

for NDMA standard solutions based on the spike of 2 ng/L

Sample No.	1	2	3	4	5	6	7	Mean Value	Std. Dev.
Sample Concentration (µg/L)	2	2	2	2	2	2	2		
Detect. con.(µg/L)	2.126	2.130	2.088	2.054	2.032	2.086	2.105	2.089	0.036

The following formula was used to determine the IDL for the instrument:

$$IDL \ = \ s \ \times \ t_{(n-1, \, \alpha)}$$ Eqn. 4.1

where: s --- standard deviation of number of spiked sample solutions;

$t_{(n-1, \, \alpha)}$ --- one-sided t-statistic appropriate for the number of samples (n) used to

determine s, at the α percent level.

Usually the 99% confidence level is selected to calculate the IDL of the analytical

method. For the 99% confidence level for 7 samples, t value was 3.143. This was used to

determine the IDL. In this case, the IDL for the analysis of NDMA in standard solution was

0.1 µg/L based on a spike level of 2 µg/L.

4.2.3 Calibration curve for standard solutions

The calibration curve was constructed by plotting the area ratio of NDMA and internal standard/surrogate versus the ratio of their internal standard/surrogate concentration at 50 ng/L of NDMA-d6 and six levels of different NDMA concentration: 2, 5, 7, 10, 50, and 100 µg/L. The concentration levels of NDMA and NDMA-d6 were chosen because in this way, the ratio of their concentrations ranged from 0.04 to 2.0. The calibration curve for the standard solutions was done again if instrument conditions changed. The calibration curve is shown in Figure 4.2 and gives a linear calibration line:

$$\frac{Peak\ Size_{NDMA}}{Peak\ Size_{NDMA-d6}} \ = \ 0.9 \times \frac{Concentration_{NDMA}}{Concentration_{NDMA-d6}} \ + \ 0.00456 \qquad \text{Eqn. 4.2}$$

Coefficient of variation is a measure of linearity of the calibration curve and the result gave a coefficient of variation of 0.999. Commonly the coefficient of variation indicates the effectiveness of the analytical method while the poor values of coefficient of variation reflected poor extraction (sometimes combined with interference) and/or poor signal saturation. The relative standard deviation (RSD), a measure of precision of an assay, refers to the absolute value of the coefficient of variation expressed as a percentage. The non-extracted calibration curve gave a Relative Standard Deviation of 16.2%.

4.3   NDMA analysis results on liquid-liquid extraction method

Applying the analytical method of liquid-liquid extraction described in the experimental section in chapter 3, NDMA analysis was assessed from several aspects.

4.3.1   Method Detection Limit (MDL) determination for the extraction standard

       Method Detection Limit (MDL) is the lowest limit that the instrument can detect

based on samples which have gone through the entire sample preparation scheme prior to

analysis and it reflects the accuracy of the instrument. Seven deionized water samples were

spiked with NDMA stock solution to give a concentration of 5 ng/L. The solutions were

extracted with methylene chloride following the extract-evaporation procedures described in

Chapter 3, and the extracted 7 samples were analyzed using GC/MS. The results are shown

in the Table 4.2.

Calibration Curve Report
File: d:\luo\2002\09\091202\ndma-varianci-sis -is.mth
Detector: 2000 Mass Spec, Address: 40

NDMA

Curve Fit: Linear, Origin: Ignore, Weight: 1/nX2
y = +0.900543x +0.004557

Resp. Fact. RSD: 16.23%
Coeff. Det.(r2): 0.998939
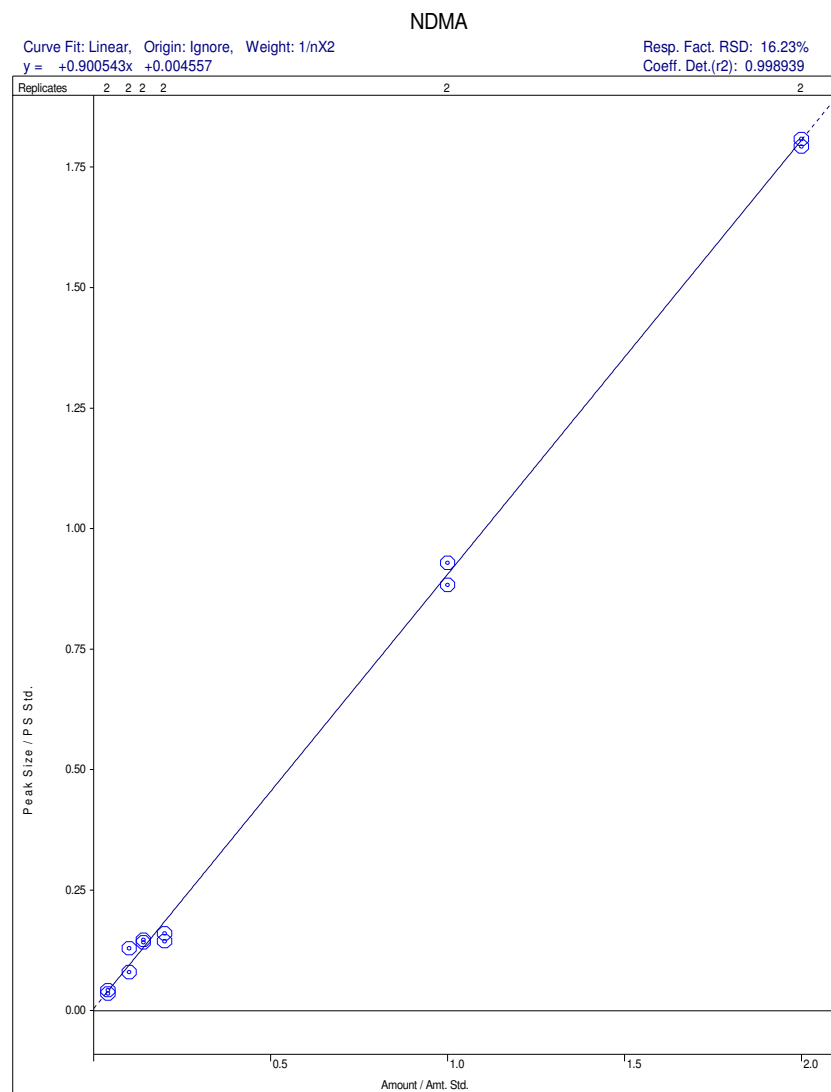
Figure 4.2. Calibration Curve of NDMA (non-extracted) with 6 NDMA levels: 2, 5, 7, 10, 50, and 100 ng/L. NDMA-d6 with concentration of 50 ng/L was used as internal standard/surrogate.

62

Table 4.2. Analysis data for Method Detection Limit (MDL) determination for

extracted solution of NDMA from DIUF water based on the spike of 5 ng/L

Sample No.	1	2	3	4	5	6	7	Mean Value	Std. Dev.
Sample Concentration (ng/L)	5	5	5	5	5	5	5		
Detect. con.(ng/L)	4.79	4.18	5.44	5.93	4.03	4.49	5.30	4.88	0.703

MDL was calculated by the equation similar to Eqn. 4.1 for the extracted solution at

the 99% confidence level and it turned out to be 3 ng/L in water. This MDL is much higher

than that of unextracted solutions which is reasonable because many factors could be causing

interferences including inorganic and organic substances and the effect of extraction of the

water samples.

4.3.2 Calibration curve for the extracted solutions

Since drinking water is the target of the project and known concentration of NDMA

in drinking water are lower than 100 ng/L, the calibration curve was extended to 100 ng/L.

The calibration curve with five levels of NDMA (20, 40, 60, 80, and 100 ng/L NDMA

solution in deionized water) standard solutions and 50 ng/L NDMA-d6 internal standard

solution was conducted by injecting the calculated amounts of NDMA and NDMA-d6 stock

solutions to the deionized water in such way that the ratio of NDMA to NDMA-d6 fell in the range of 0.1 to 2.0. Following the extract-evaporation procedure, the 5 samples were analyzed using GC/MS. The obtained calibration curve is shown in Figure 4.3 and the equation is shown as Eqn. 4.3.

$$\frac{Peak\ Size_{NDMA}}{Peak\ Size_{NDMA-d6}} = 1.05 \times \frac{Concentration_{NDMA}}{Concentration_{NDMA-d6}} + 0.146 \qquad \text{Eqn. 4.3}$$

The coefficient of variance (r^2) of the obtained calibration curve was 0.993 and Relative Standard Deviation (RSD) of 14.6%. Compared with the one obtained from non-extraction solution, this one has a lower coefficient of variance which is normal since extraction procedure and interferences from water sample affect the analysis result.

Calibration Curve Report
File: d:\luo\2002\10\1023\ndma-varianci-sis -is-3.mth
Detector: 2000 Mass Spec, Address: 40

NDMA

Curve Fit: Linear, Origin: Include, Weight: 1/nX2
y = +1.046547x +0.145582

Resp. Fact. RSD: 14.20%
Coeff. Det.(r2): 0.992666

Replicates   1   1   1   1   1
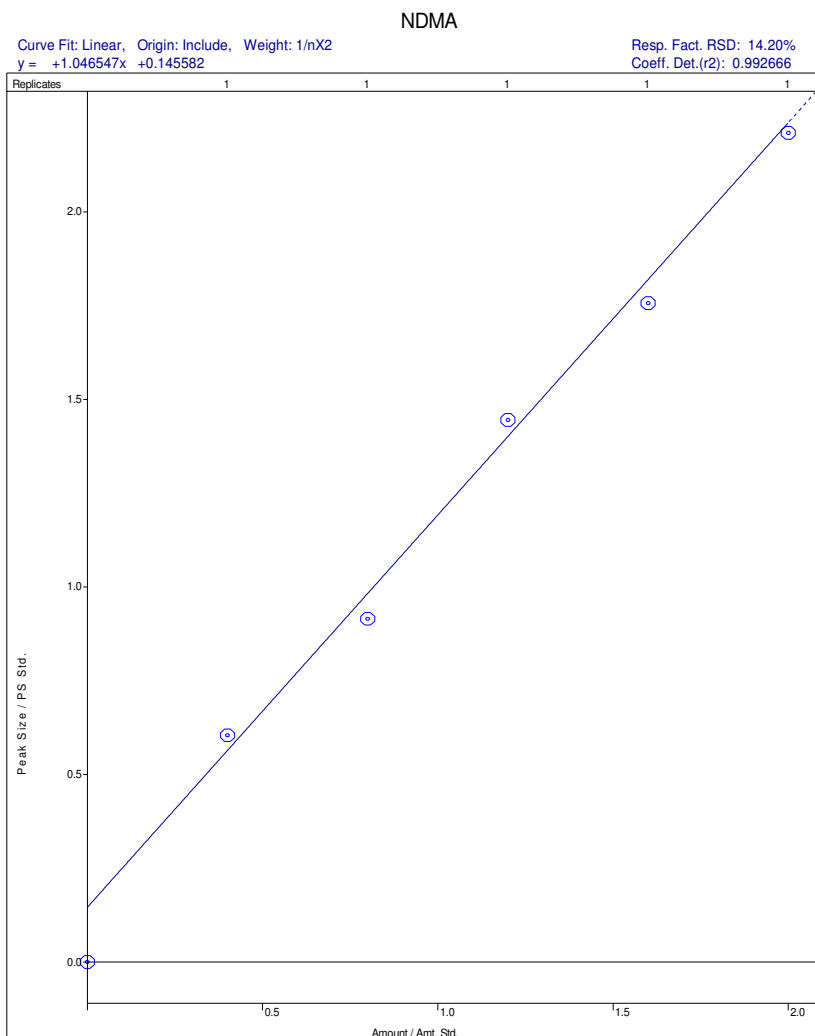
Figure 4.3. Calibration Curve of NDMA using Liquid-liquid extraction with 5 NDMA

levels: 20, 40, 60, 80, and 100 ng/L. NDMA-d6 with concentration of 50 ng/L was used as

internal standard/surrogate.

4.3.3   Efficiencies of extraction

The recovery of liquid-liquid extraction with separatory funnel generated up to 30% recovery for NDMA. Usually the recovery ranges from 15% to 25%. This result is similar to that of traditional liquid-liquid extraction method (Yoo and Fitzsimmons, 2000).

4.3.4   Quality control

To ensure the validity of the analysis results, quality control including calibration blank, calibration curve check, duplicate and spike samples were analyzed for every ten water sample analysis or for each analytical batch.

Calibration blank is aqueous solution that is prepared with the same volume of chemical reagents used in the preparation of the calibration standards and diluted to the appropriate volume with the same solvent (water or organic) used in the preparation of calibration standard. The calibration blank is used to give the null reading for the instrument response versus concentration calibration curve. In this analytical method, calibration blank was made by adding calculated amount of NDMA-d6 to 1 liter of DIUF water as an internal standard/surrogate to make the concentration of 50 ng/L to ensure the efficiency of the procedures. The analytical results showed that the calibration blank usually was lower than 2 ng/L which was lower than the MDL.

Calibration check, also called as Continuing Calibration Verification (CCV), is also an important factor in the chemical analysis and quality control which is the verification of the ratio of instrument response to analyte amount. In the LLE method for NDMA analysis, the calibration check was made by adding calculated amount of NDMA and NDMA-d6 stock solutions to 1 L of DIUF water, processing with the same procedures including extraction

procedures described in the liquid-liquid extraction method and GC/MS analysis and compare the result with the same concentration level on the calibration curve. In the study of NDMA analysis, concentrations of 50 ng/L on both NDMA and NDMA-d6 were used as calibration check and the deviation of NDMA results of each run on calibration check was less than 10%.

Duplicate refers to a second aliquot of a sample that is treated the same as the original sample in order to determine the precision of the analytical method. In this study, duplicate samples were randomly selected and NDMA-d6 stock solutions was added to the duplicate water samples to make the concentration of NDMA-d6 as 50 ng/L and came out the deviation to the original sample was usually lower than 20%.

Matrix spike samples are employed to evaluate the effect that a particular sample matrix has on the accuracy of a measurement. A matrix spike sample is prepared by adding a known amount of the target analyte to a second aliquot of a sample that is treated the same as the original sample and compare the result to that of the original sample. The recovery of the matrix spike is calculated using the following formula:

$$ Y,\% \quad = \quad \frac{A_{ms} - A_{fs}}{A_a} \quad \times \quad 100 \qquad \text{Eqn. 4.3} $$

where A_{ms} = the amount of target analyte measured in the matrix spike sample

A_{fs} = the amount of target analyte measured in the corresponding original sample

A_a = the amount of target analyte spiked (into the matrix spike sample)

The recovery of a matrix spike provides an indication of how efficient the analytical procedure was for the particular samples/sample matrix used for the matrix spike and the ability of the test procedure to generate a correct result. So the analytical accuracy can be assessed from the recovery of spike samples. During the NDMA analysis throughout the experiment, the second aliquot was selected randomly and calculated amount of NDMA and NDMA-d6 stock solutions were added to the water sample to make the added concentrations for both chemicals to be 50 ng/L. The recoveries of the matrix spike sample fell in the range of 80-120%.

4.4   NDMA analysis results on solid phase extraction method

Solid phase extraction method was conducted and results are presented and evaluated in the following sections.

4.4.1   Calibration curve and Method Detection Limit

Same as the LLE method, calibration curve for the solid phase extraction was extended up to 100 ng/L because NDMA concentration in most drinking water and its source are generally lower than this level.

As shown in Figure 4.4, the obtained calibration curve by solid phase extraction fits linearity very good with the coefficient of variance (r^2) higher than 0.996 and Relative Standard Deviation (RSD) of less than 5%.
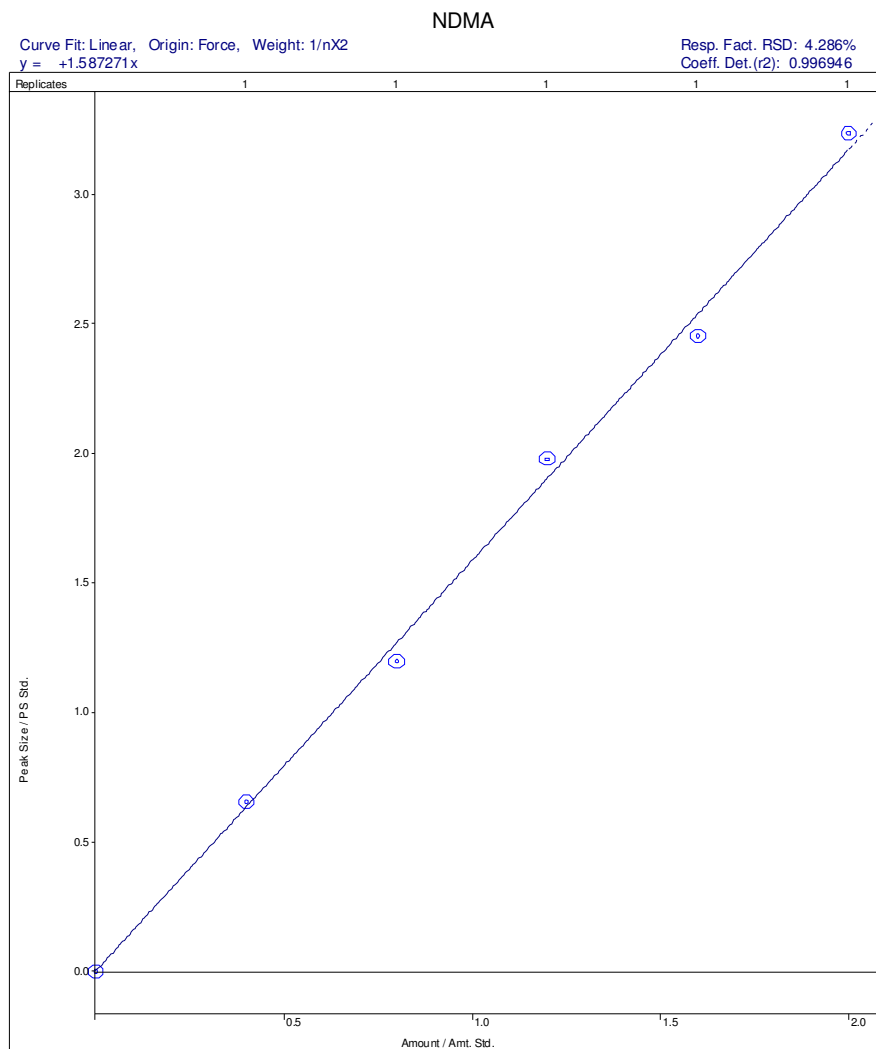
Figure 4.4. Calibration curve applying Solid Phase Extraction (SPE) method with 5 NDMA

levels: 20, 40, 60, 80, and 100 ng/L. NDMA-d6 with concentration of 50 ng/L was used as

internal standard/surrogate.

Method Detection Limit study was based on 7 replicates analysis of deionized water spiked with 5 ng/L NDMA after solid phase extraction procedures described in the experimental section. The calculated MDL for the 7 replicates based on 5 ng/L NDMA spike for 99% confidence level was 1 ng/L.

4.4.2   Efficiencies of extraction

The efficiencies of Solid Phase Extraction in this study can reach up to 65%. Generally over 50% was obtained by applying Solid Phase Extraction. Compared to about 20% recovery by the Liquid-Liquid Extraction as discussed earlier, this value is much higher.

4.4.3   Quality control

Quality control including calibration blank, calibration check, duplicates and matrix spike were conducted on each analysis run or every ten water samples. For method blank, most were 2 ng/L NDMA concentration or below by using DI water. However, sometimes high concentrations of NDMA were detected in DI water (up to 29 ng/L). These high concentrations of NDMA were usually detected in DI water coming from the old DI tank. When the tank was changed, the calibration blank was detected to have NDMA lower than 2 ng/L. DIUF water was also used for the quality control process and the calibration blanks were lower than 2 ng/L. The high concentrations of NDMA in DI water may be related to the resin used in DI water tanks. It contains amines that can serve as NDMA precursors. The recoveries of calibration check, matrix spike and sample duplicates are 90%, 80-120% and 90%, respectively.

4.5   Comparisons between LLE and SPE

NDMA analysis in natural water and drinking water using liquid-liquid extraction method and solid phase extraction were compared and assessed and an optimal analytical method was determined based on this assessment.

4.5.1   Analytical results of both methods

From the analysis results demonstrated in the above sections, solid phase extraction method has better results compare to the liquid-liquid extraction method. As for method detection limit, analysis from SPE has lower MDL of about 1 ng/L while this results from LLE was 3 ng/L. Results from SPE has better linearity of calibration curve as its coefficient variation was 0.996 and RSD was 4.6% versus the 0.993 and 14.6% from LLE. SPE also has better results on quality controls. It has lower calibration blank, higher recovery of calibration check, matrix spike and duplicates compare to LLE.

4.5.2   Analytical method efficiency

The method efficiency from LLE in this study was approximately 20% recovery of NDMA which is similar to the results of 20% to 30% of the recovery presented by the modified LLE followed by GC/High Resolution Mass Spectrum (Yoo, et al., 2000). The SPE can give a NDMA recovery of typically over 50% and up to 65%.

4.5.3   Experimental conditions

From the extraction procedures, LLE was very complicated, laborious and took long time. It required vigorous shaking during extraction and a long rotary evaporation by

71

nitrogen gas blowing off. Since the extraction was done manually, the time spent on the extraction procedure for every sample put limitation on the number of samples that could be analyzed during a set period of time. Typically, it would be 2 days to have 10 samples extracted by LLE method, while it would only required 5-6 hours by SPE method. One problem with the SPE method was that during the extraction procedure, the Ambersorb 572 beads sometimes broke and the fractions of beads caused blockage in the column of the GC/MS when injecting samples into the GC/MS.

4.5.4 Solvent usage

Applying liquid liquid extraction method, about 200 mL methylene chloride would be consumed while only 0.5 mL methylene chloride would be used by applying solid phase extraction method. Since methylene chloride is an irritating organic material and it would eventually go to the environment, SPE method will cause much less burden on the environmental.

In summary, from the discussion above, it can be seen that SPE method is more favorable and practical for the detection of low concentration of NDMA in water from many aspects.

4.6   Summary

The analytical methods for the analysis of N-nitrosodimethylamine (NDMA) in drinking water samples for measurement in the part per trillion ranges were developed. The Liquid-liquid extraction (LLE) method and Solid phase extraction (SPE) method were applied in the extraction procedure coupled with ion trap mass spectrometer (MS) with chemical ionization (CI) in the mode of selected ion storage (SIS). Analytical results from two extraction methods were compared and evaluated. Solid phase extraction with GC/MS/CI/SIS instrument analysis method presented a reliable, accurate, practical, and cost-effective procedure for the routine analysis of NDMA at a trace level in drinking water samples.

CHAPTER 5

OCCURRENCES OF NDMA

IN MISSOURI DRINKING WATER

5.1   Introduction

In order to investigate the occurrence of NDMA in Missouri drinking utilities, ten water utilities using chloramines as primary or secondary disinfectants were selected to determine NDMA levels. Chloramines were believed to be an important precursor of NDMA.

5.2   Descriptions on selected Missouri water utilities

Water samples were collected from ten drinking water utilities using monochloramine as their primary disinfectants. General information on these ten utilities including number of people served by the utility, flow rate, TOC, alkalinity, chemicals and dosages to provide ammonium and chlorine, residual chlorine or chloramines, TOC, TTHM and HAA5 were reported if available. Some general information of these utilities are listed in Table 5.1.

5.2.1   *Jefferson County Water Treatment Plant*

Jefferson County Water Treatment Plant uses Big River as water source. This 1.1 to 1.5 MGD utility services 1,700 customers in Jefferson County area. TOC concentration ranges from 3.0 to 4.5 mg/L. Alkalinity is 176 to 200 mg/L as $CaCO_3$. About 50 lbs chlorine and 50 lbs ammonia sulfate are used everyday as a disinfectant. In summer, more ammonium

sulfate is used. For the treated water, the chlorine residual is about 3.00 mg/L and TOC

concentration is about 2 to 3 mg/L on average. TTHM and HAA$_5$ are 30 µg/L and 15.0 µg/L,

respectively.

5.2.2   *Kirkwood Water Treatment Plant*

Kirkwood water treatment plant serves 30,000 to 40,000 people with capacity of

2.5MGD. It takes 2% surface water and 98% well water as water source. Sometime in

summer, the percentage of surface water would go as high as 40% with the water demand

going up. The utility uses chloramines as primary disinfectant. About 70 to 80 lbs chlorine

and 27 lbs of ammonia sulfate are used every day. The treated water has a chlorine residual

of 1 to 1.5 mg/L in general, and average 2.4 mg/L in summer.

5.2.3   *Howard Bend Water Treatment Plant, St. Louis County*

Water utility of Howard Bend uses Missouri River as its raw water source.

Monochloramine obtained by adding gas chlorine into water followed by liquid ammonium

is used as disinfectant in the disinfection process. The distributed water has average 2.5 mg/L

chloramines residual.

5.2.4   *Chain of Rocks Water Treatment Plant*

Chain of Rocks Water Treatment Plant is located near St. Louis city, Missouri and

uses Missouri River and Mississippi River as its water source. Gas chlorine and 19% aqueous

ammonia are added into water to the water to form chloramines and to serve as disinfectant in the process. The distributed water has 2.5 to 2.75 mg/L residual of chloramines.

5.2.5   Sedalia Water Treatment Plant

Sedalia water treatment plant serves about 20,000 people for Sedalia with capability of 2.2 MGD. It usually uses 36% lake water and 64% ground water as water sources. The utility is increasing the percentage ground water at present time. They use 75 to 100 lbs chlorine and 50 lbs of ammonium sulfate everyday. On an average, the treated water has a chlorine residual of 2.5 mg/L.

5.2.6   Jefferson City Water Treatment Plant

Water utility of Jefferson City uses Missouri River water as water source. The utility uses chlorine as a primary disinfectant and then ammonium sulfate is added in the clear well to form chloramines.

5.2.7   Clarance Cannon Water Treatment Plant

Water utility of Clarance Cannon takes surface water from Mark Twain Lake as water source. The utility uses gas chlorine and gas ammonia to get chloramines as a primary disinfectant. Its final water has a residual of chloramines at the level of 2.5 to 3 mg/L.

5.2.8   Independence Water Treatment Plant

Independence Water Treatment Plant uses well water from alluvial plain as its water source. Liquid chlorine and ammonia gas are added into the water to the water to get chloramines which serves as disinfectant. Chloramines are kept at 2.0 mg/L as a residual in the distribution water.

5.2.9   Tri-County Water Treatment Plant

Well water from alluvial plains is used as water source in Tri-County water treatment plant. The ammonia exists in the raw water which served as ammonia source for chloramine disinfection combined with gas chlorine. The residual of chloramines is kept at the level of 2.4 to 2.8 mg/L.

5.2.10   Kansas City Water Treatment Plant

Kansas City water treatment plant takes Missouri River as its water source. Gas chlorine and liquid ammonia are added into water to form chloramines to serve as disinfectant. The final water generally kept the residual of chloramines at the level of 2.0 to 2.2 mg/L.

Table 5.1. General properties and sources of water samples in the NDMA occurrences study in Missouri

	Location	Source of raw water	Chemical added to provide N	Conc.of NH_4^+ (mM)	Chemical added to provide Cl	Conc.of Cl_2 (mM)	Cl_2:N	Residual chloramine (ppm)	DOC (mg/L)
1	Independence	Ground water	gas ammonium	0.0235	liquid Cl_2	0.035	1.49	2	1.96
2	Kirkwood	surface + ground water	Granular ammonium sulfate	0.0105	gas Cl_2	0.0779-0.0974	7.43-9.29	3	0.75
3	Clarance Cannon	Surface water	gas ammonium	*	gas Cl_2	*	*	2.5-3.0	5.48
4	Tri-County	Ground water	Existing ammonium in raw water	0.1	gas Cl_2	0.146	1.46	2.4-2.8	2.52
5	Kansas City	Surface water	liquid ammonium		gas Cl_2	0.024		2-2.2	2.98
6	Jefferson County	Surface water	Granular ammonium sulfate	0.048	gas Cl_2	0.113-0.0767	1.60-2.34	2.5	1.66
7	Howard Bend	Surface water	liquid ammonium	0.056-0.127	gas Cl_2	0.0338	0.27-0.60	2.5	3.86
8	Jefferson City	Surface water	Granular ammonium sulfate	0.0106	12.5% liquid Cl_2	0.006 - 0.007	0.57-0.66	2.4	3.725
9	Chain of Rocks	Surface water	19% aqueous ammonium	0.0134-0.0268	gas Cl_2	0.042	1.57-3.13	2.5	5.22
10	Sedalia	36%surface + 64%groundwater	liquid ammonium	0.088	gas Cl_2	0.056	0.64	2.3-2.4	6.99

5.3   Analytical results in detecting occurrences of NDMA in Missouri

By using the SPE-GC/MS analysis method described in Chapter 3, the analysis
results for eleven water samples are listed in Table 5.2. It showed that NDMA did occur in
Missouri water utilities using chloramines as a disinfectant. The NDMA concentrations in
Sedalia, Chain of Rocks, Jefferson City and Howard Bend's finished water were above 10
ng/L set as an action level by CDHS and all four utilities use chloramines as primary or
secondary disinfectants. These results indicated that chloramines could be the cause of
NDMA formation in drinking water plants.

Table 5.2. NDMA Analysis Results by solid phase extraction method (SPE) in Missouri

Drinking Water Utilities

Water Sample	Water Source	DOC (mg C/L)	NDMA (ng/L)
Sedalia	Lake water + ground water	6.99	29
Chain of Rocks	River water	5.22	24
Jefferson City	River water	3.72	16
Howard Bend	River water	3.86	14
Jefferson County	River water	1.66	7
Kansas City	River water	2.98	6
Tri-County	ground water	2.52	5
Clanrance Cannon	Lake water	5.48	4
Kirkwood	Ground water+ surface water	0.75	3
Independence	ground water	1.96	3

Note: Action level set by California Department of Health and Services (CDHS) is 10 ng/L

for NDMA in drinking water.

In addition NDMA was monitored in the Sedalia finished water over one and half year period (Figure 5.1). Unfortunately it is difficult to interpret these results because the Sedalia water was from a mixture of surface water and ground water. The ratio of surface water to ground water is often changed due to supply, contamination and other issues. . Ratios were not available for this study. Without more data on the ratio of ground water to surface water in its water source, seasonal changes cannot be determined.
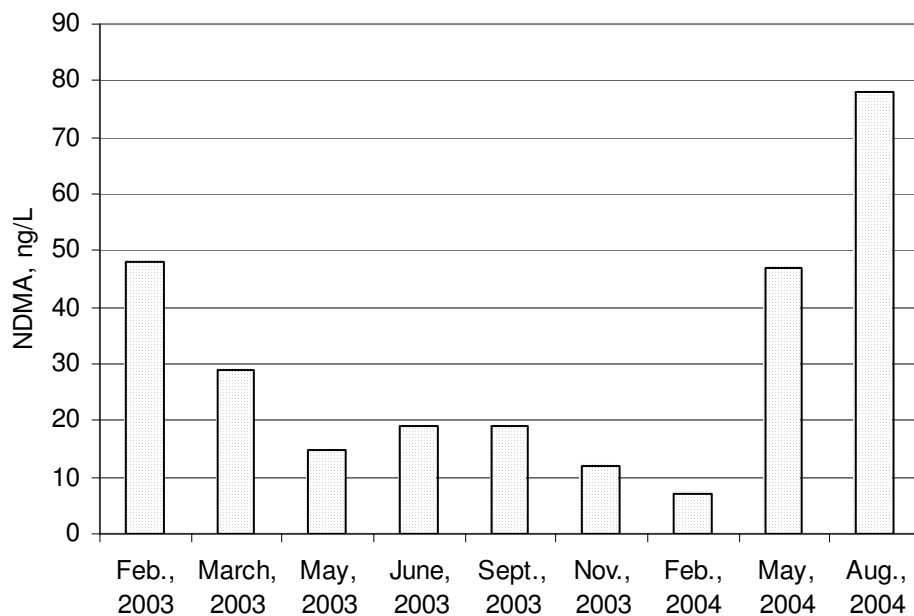
Figure 5.1. NDMA occurrences in Sedalia water samples

5.4   Comparisons of analytical results with commercial lab

Water samples from Sedalia water treatment plant and Columbia water treatment plant were analyzed for the cross check by both Liquid Liquid Extraction and Solid Phase Extraction method in Missouri Water Resources Research Center (MoWRRC). The same samples were stored in 1-L precleaned amber bottle and excess ascorbic acid was added to all

samples to assure no more chlorine or monochloramine were left in the sample and the

NDMA formation in the sample ceased. These samples were sent out to a commercial lab-

Weck Lab in California to be analyzed by using Liquid Liquid Extraction followed by the

sample analysis on the ThermoFinnigan GC/MS model Trace DSQ (Dual-Stage

Quadrupole). Together with these water samples, a known concentration of NDMA with 50

ng/L in solution was analyzed to check the validity of the analysis results. The results are

presented in Table 5.3.

     Results of the water sample of Columbia showed no NDMA was detected, from both

labs and both extraction methods. For the analysis validity check with 50 ng/L NDMA

concentration, the MoWRRC came out with the closest result of 48 ng/L by SPE method, and

46 ng/L by LLE, while the Weck Lab gave the result of 42 ng/L of NDMA by LLE. These

results were all less than the expected result, but differences among these analysis results are

less than 15% and their deviations from the expected result were all less than 20% and were

acceptable for their validity.

     Results on the water sample of Sedalia water treatment plant from different labs and

different extraction methods are shown in Table 5.3. Result from Weck Lab using LLE

method had the highest result on NDMA detection of 54 ng/L which was close to the result

from MoWRRC with the NDMA concentration of 48 ng/L using the SPE method while the

result from MoWRRC with the NDMA concentration was 36 ng/L using LLE method. The

results were within the acceptable deviation of 20%.

Table 5.3. Cross check by different labs and different analytical methods on two water

samples in Missouri

Water Utilities	Concentration of NDMA (ng/L)		
	MoWRRC***	MoWRRC	Weck Lab****
	LLE	SPE	LLE
Sedalia	36	48	54
Columbia	ND**	ND**	ND**
Sample Check*	46	48	42

Note: *: A solution with a 50 ng/L of NDMA made to check analysis

**: ND represents not detected

***: Missouri Water Resources Research Center

****: Weck Lab uses LLE analytical method to detect NDMA

5.5   Relationship between DOC and NDMA yield in natural water

Comparing the NDMA results in Missouri water utilities (Table 5.2) and water

sample characteristics in Table 5.1, some conclusions could be made. First, water sources

seem to be a factor in influencing NDMA formation. In most water treatment plants that use

ground water as source water, NDMA formation concentrations were lower than other plants

and below the California standard of 10 ng/L. For surface water, NDMA formation levels

were generally higher. Among the four water samples detected with NDMA concentrations

higher than 10 ng/L, three of them used surface water as source water while the other one,

Sedalia, used mixture of 36% surface water and 64% ground water as its source. Clarance

Cannon is another exception that used surface water as its source while its NDMA formation was low.

Other parameters of the water treatment including concentration of chemicals that provided for N and Cl, their ratio, and residual chloramine concentrations are also listed in Table 5.1. However no other direct relationship was found between them and NDMA formation.

Dissolved organic carbon (DOC) was measured for ten water samples as a parameter of water and was listed with NDMA concentration also in Table 5.2. NDMA concentrations in water were higher with incresing DOC concentration although exceptions occurred (Figure 5.2 and Figure 5.3.). One example was Clarance Cannon. It had a DOC level of 5.48 mg C/L while its NDMA occurrence was only 4 ng/L. From the relationship between DOC and NDMA formation in 10 water samples (Figure 5.3), a comparatively strong correlation was observed (r^2=0.61). Gerecke and Sedlak (2003) investigated the relationship between NDMA formation potential (NDMAFP) and DOC and reported a weak correlation (r^2=0.41).

DOC is a measurement parameter of natural organic matter which is a very complicated aggregate of organic compounds with relatively unknown structures and chemical composition. Different correlation between two parameters from different sample sources also indicate that DOC has an important role in the NDMA formation, however, the effective role in the NDMA formation may not be the natural organic matter as a whole but just some specific part. The different characteristics of natural organic matter may have different potential to form NDMA in natural water samples.

NDMA and DOC of Water Samples in Missouri
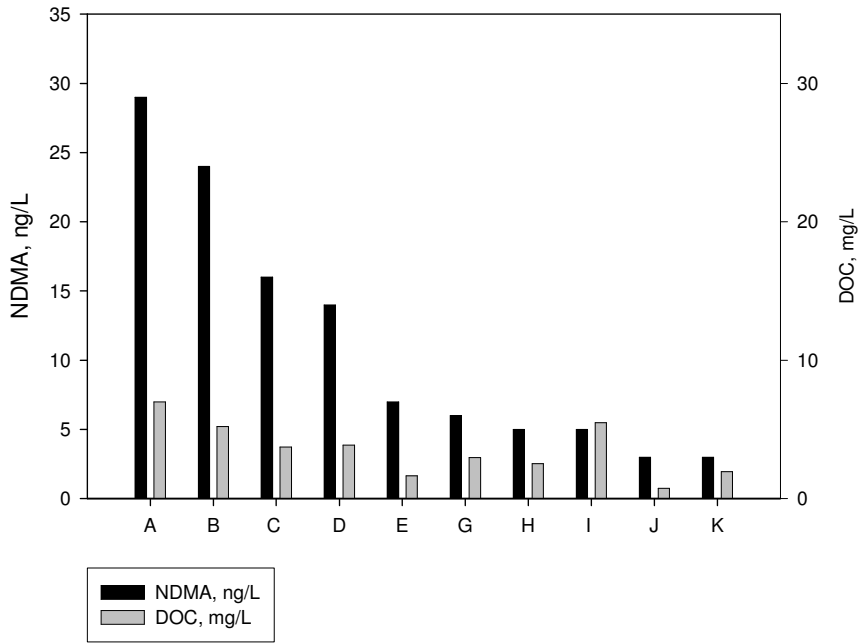
Figure 5.2. NDMA concentration level and DOC for 11 water treatment plants in Missouri

$y = 3.7179x - 1.8648$

$R^2 = 0.6084$
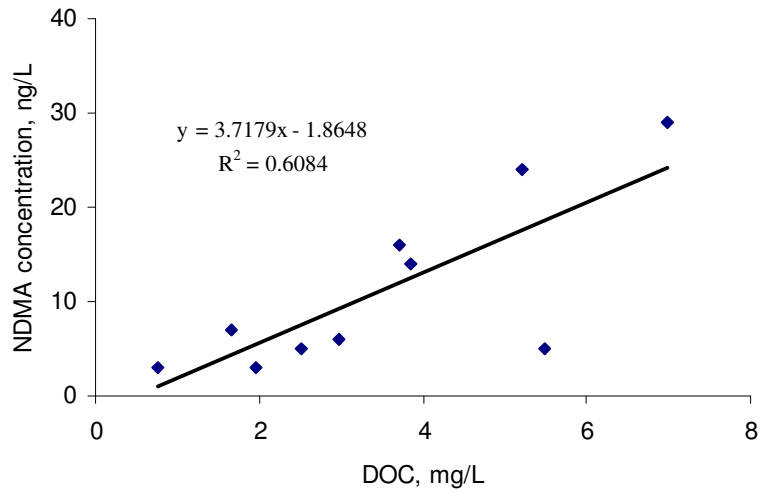
Figure 5.3. NDMA concentration relates to DOC content

for 10 water samples from utilities in Missouri

5.6   Summary

     The developed analysis method was applied in the analysis of NDMA in ten drinking water utilities in Missouri which used monochloramine as a primary disinfectant. Four utilities were found to have NDMA higher than the 10 ng/L action level set by California Department of Health and Services. The detected NDMA levels in these utilities indicated that DOC played an important role in the NDMA formation in natural waters.

CHAPTER 6

ROLE OF NOM IN THE FORMATION OF NDMA

6.1   Introduction

The results from the NDMA occurrences in Missouri water treatment plants indicate significant concentrations of NDMA existing in drinking water from water plants applying monochloramine as a disinfectant. Current NDMA formation studies in the literature have been focused on specified precursors such as DMA and other chemicals with similar functional structure (Choi and Valentine, 2002 &2003; Mitch and Sedlak, 2003 & 2004). However, NDMA yields from these known precursors could only account for 10 % of the total amount detected in the chloramination of secondary wastewater effluent (Mitch and Sedlak, 2002). In a study of NDMA formation from DMA in natural waters, it was also found that the maximum theoretical concentration of NDMA formed from DMA was much lower than the measured NDMA concentrations (Gerecke and Sedlak, 2003). Precursors of DMA can not explain the detected high level of NDMA in natural waters and very few reports were published on its formation in natural waters. The results from Chapter 5 reported results of studies on the more ubiquitous and reactive accumulations of natural organic matters in natural waters which have recognized reactivity with disinfectants as free chlorine and monochloramine.

This chapter reports on study of NDMA formation potentials in natural waters and role of natural organic matter in the formation of NDMA in natural waters. Kinetics of NDMA formation and effect of pH are also discussed in this chapter.

6.2   Degradation of monochloramine

A stock solution of monochloramine with 100 mM concentration was prepared every time before the NDMA formation experiment. A test on the stability of the monochloramine stock solution was conducted and data are shown in Table 6.1 and Figure 6.1. It can be seen that the monochloramine stock solution was stable after its preparation for the first two hours and then its concentration decreased. After about 20 hours of its preparation, its concentration decreased dramatically. This could be explained by the decomposition and disproportionation reactions of monochloramine as shown in Eqn. 2.3, Eqn. 2.5 and Eqn. 2.6. Decrease in pH value during the process of monochloramine degradation indicated that acid production involved as shown in Eqn. 2.6.

$$NH_2Cl + HOCl \rightarrow NHCl_2 + H_2O \qquad \text{Eqn. 2.3}$$

$$2\,NH_2Cl \rightarrow NHCl_2 + NH_3 \qquad \text{Eqn. 2.5}$$

$$2\,NH_2Cl + HOCl \rightarrow N_2 + 3HCl + H_2O \qquad \text{Eqn. 2.6}$$
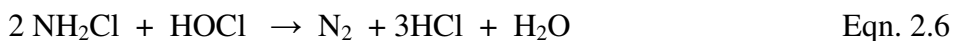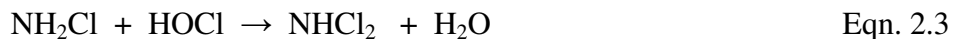
So it was better to analyze the monochloramine concentration every time before adding it to the water samples to do the NDMA formation reactions. It was also better to use the freshly made monochloramine within 2 hours of its preparation; otherwise the volume of monochloramine needed for the reaction would have been changed to obtain the same concentration.

The degradation experiment of monochloramine at low concentration level was also done and is shown in Figure 6.2. It was stable for the first two days (48 hours) and the

concentration of monochloramine only decreased by 4% (from 1 mM to 0.96 mM) and after

that it decreased greatly and after 7 days (146 hours), it was only 75% of its original one.

Table 6.1. Degradation of Monochloramine after formation

Time (hr)	pH	NH_2Cl concentration (mM)
0.25	9.9	78.87
1.6	9.8	80.38
6.75	9.5	76.06
21.5	9	62.35
24.3	8.8	63.10
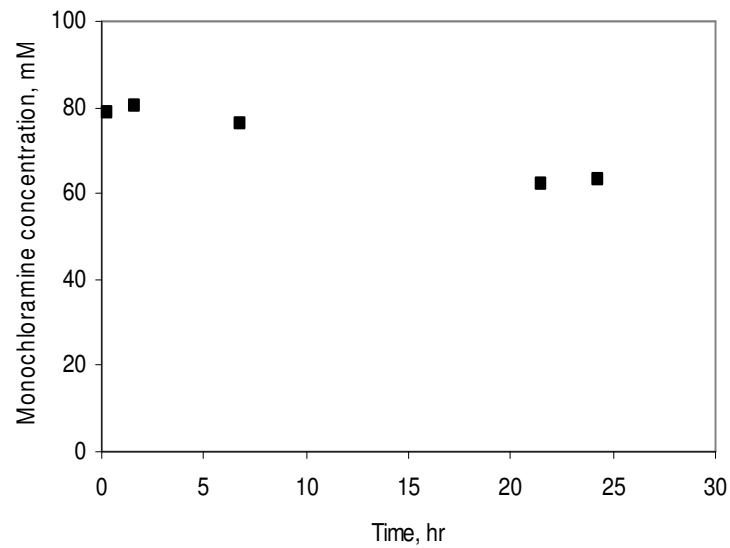
Figure 6.1. Monochloraime degradation at high concentration level
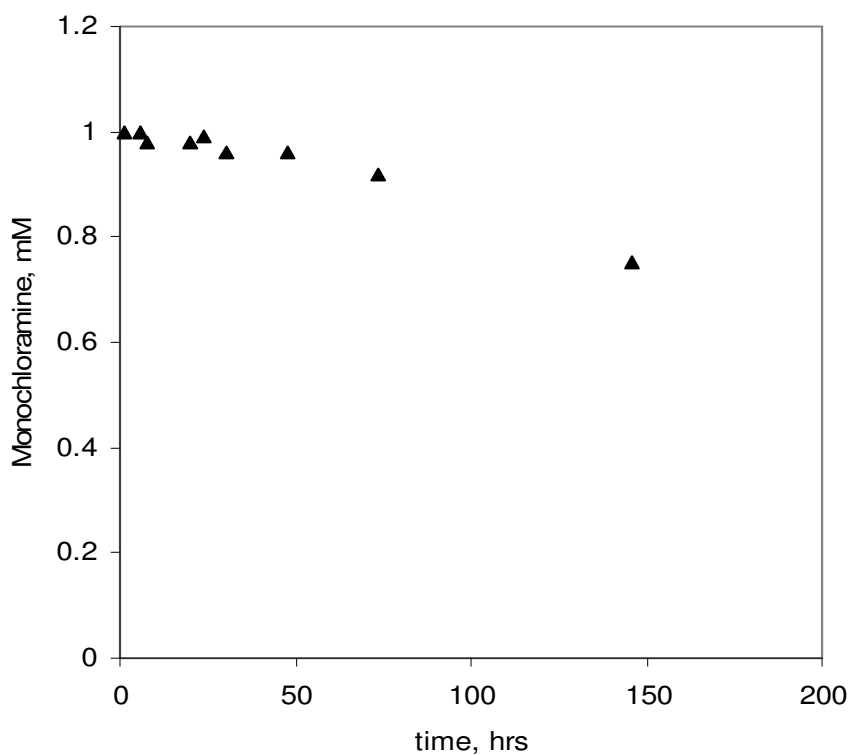
Figure 6.2. Monochloramine degradation at low concentration level of 1 mM in DIUF water

6.3   NDMA formation in ultrafilter deionized (DIUF) water

NDMA formation in NDMA-free DIUF water was conducted with two monochloramine levels and lasted for up to 220 hours: The high monochloramine concentration was 1 mM and the low concentration was 0.1 mM. The data are shown in Figure 6.3.

For the high level of monochloramine solution, NDMA yield increased with the reaction time although the total difference after 220 hours was not higher than 10 ng/L. There existed variations to the inclination and this maybe due to analysis, since the overall NDMA concentrations were low, this variation was reasonable. The total NDMA formed after 220 hours was 11 ng/L. This indicated that monochloramine could also produce some NDMA in

DIUF waters even though the amount was small. The rate of NDMA formation was higher

for the first 48 hours and then became flat as time increased.

For the low level of monochloramine solution, only NDMA formations for 1, 24, and

48 hours were tested. An increasing trend in NDMA concentration with reaction time was

also observed (Figure 6.3).
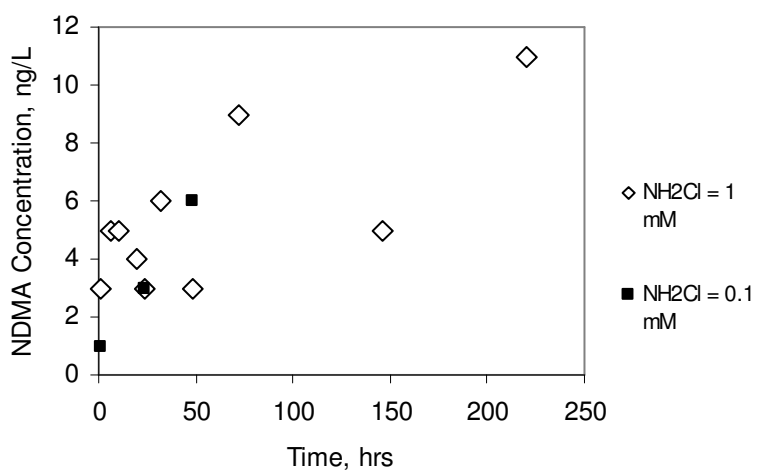
Figure 6.3. NDMA formation in DIUF water at two monochloramine levels:

1 mM and 0.1 mM.

6.4   NDMA formation in raw water samples

NDMA occurrences in Sedalia water treatment plant were observed to be the highest

in a previous study and became the main focus of the NDMA formation study. The raw water

samples from Sedalia and water treated after the sedimentation process from the water

Treatment Plant were collected and reacted with high monochloramine levels for up to two

days (48 hours). A water sample from the effluent was also collected and compared with the

NDMA concentration formed under high monochloramine level.

The results in Figure 6.4 show that with excess monochloramine existing, NDMA could be formed at a concentration levels much higher (15 ng/L higher) than the effluent from the plant (18 ng/L of NDMA, data did not shown in Figure 6.4). Sedalia raw water could yield as high as 33 ng/L after 1 hour of contact with 1 mM monochloramine. After that, it still increased but with a lower rate until after 2 days reaction the NDMA yield reached 52 ng/L.

The other water sample was collected at the place after sedimentation treatment but before first addition of chlorine in the water utility. The only difference between two samples was the process of sedimentation. From Figure 6.4, the NDMA yield from this water sample after 2 days (48 huors) reaction with 1 mM monochloramine was 32 ng/L. There was a 20 ng/L difference of NDMA formed in two samples. This fact indicated that part of NDMA precursors in Sedalia water samples could be removed by the process of sedimentation treatment.
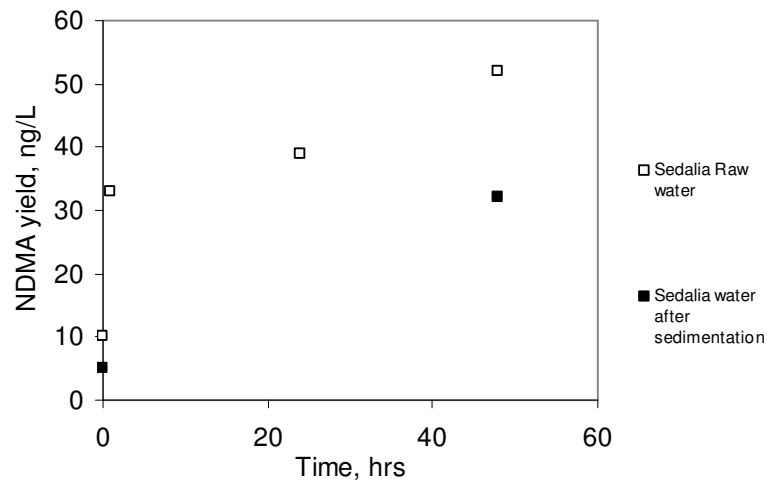
Figure 6.4. NDMA formation in Sedalia water samples applying

1 mM monochloramine as oxidant.

A raw water sample from local Columbia drinking water plant was collected reacted with 1 mM monochloramine for up to 48 hours. The NDMA level detected was 14 ng/L and was much lower than both samples from Sedalia water plant. This suggested that NDMA yields not only was related to disinfectant but also with the water characteristics of the water source. Hence, water from Sedalia water plant became the main focus of the study on NDMA formation.

6.5   Fractionation in natural water

Results from NDMA occurrences study showed some relationships between DOC contents and NDMA formation in effluent of water plants while results from NDMA formation potential study on both Sedalia raw water and Columbia raw water indicated water characteristic may play an important role in NDMA formation in natural water. Since DOC is a typical characteristic of natural organic matter (NOM) and NOM has been determined to be very active in the formation of other disinfection by-product of free chlorine (TTHM and HAAs), NOM was studied with relationship to NDMA formation.

As a complementary approach to studying whole water samples, isolating functionally distinct DOC fractions from natural waters to determine fundamental chemical properties of each fraction, ultimately relating structural and chemical properties to their environmental roles was used. Several separation techniques were used for the isolation of organic solutes from water. A technique of XAD-8 and XAD-4 resins used in tandem as shown in Figure 3.1 was applied to isolate different organic fractions in the raw water samples from Sedalia water treatment plant. The filtrated water sample was acidified to pH 2

93

and passed through the XAD-8 resin. The hydrophobic fraction containing the humic substances (mainly contains fulvic acids, humic acids, and hydrophobic neutrals) was retained on the resin and thus separated from water samples. The effluent from polar XAD-8 resin contained hydrophilic acids, bases and neutrals and was passed through XAD-4 resin subsequently. Hydrophilic acids were then adsorbed onto the more hydrophobic XAD-4 resin and were called the transphilic fraction. The hydrophilic bases and neutrals remained in the water after passing through the XAD-4 resin and were called the hydrophilic fraction. Three fractions were thus separated in solutions according to their hydrophobic property.

The DOC values for Sedalia water samples and the isolated fractions are listed in Table 6.2. The XAD-8 resin adsorbed 59% of the total DOC (5.03/8.71) resulting in a hydrophobic/hydrophilic separation of 59%/41%. This percentage of hydrophobic fraction removed on XAD-8 resin is common in natural waters especially in those waters with high concentrations of fulvic and humic acids. Generally, this fraction of water accounts for the 30-50% of the total DOC in natural waters.

The XAD-4 resin adsorbed about 21% (1.84/8.71) of the DOC from effluent of XAD-8 resin (transphilic fraction). Only 20% (1.72/8.71) of the DOC as hydrophilic neutrals and bases (hydrophilic fraction) remained in the effluent of XAD-4 resin. Typical reported transphilic fractions were 7-30% (Thurman, 1986; Aiken et al, 1992) and the hydrophilic fractions were about 20% (Thurman, 1986). The total DOC recovery of about 98.6% indicated a good recovery for this fractionation process.

Table 6.2. DOC results of Sedalia Raw Water fractionation

Water Sample	DOC (mg/L)
Sedalia Raw water before filtration	8.13
Sedalia Raw water after filtration	8.71
Hydrophilic fraction	1.72
Hydrophobic fraction	5.03
Transphilic fraction	1.84
Recovered DOC (mg/L)	8.59
Fractionation Recovery (%)	98.6
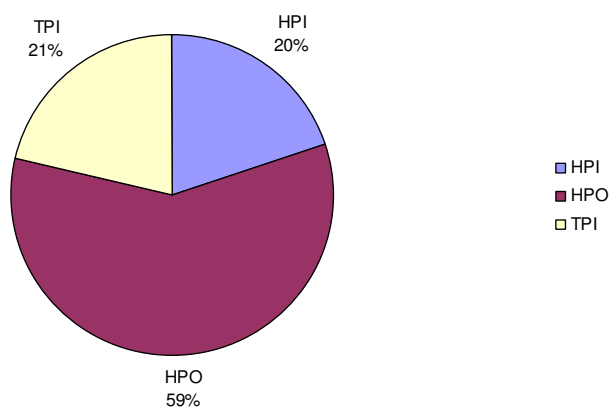
Figure 6.5. Recovered DOC proportions of three

fractions from Sedalia raw water sample.

A second water sample was collected from Sedalia water plant and the fractionation was conducted on the sample. The results are also shown in Table 6.3. From this sample, the total recovered DOC was about 95.4% (6.67/6.99) of the total DOC of the filtered water sample. This was a little lower than the one obtained previously (98.6%) which was in the acceptable range considering the complex procedures for separation and recovery processes.

Among the three separated fractions, the recovered hydrophobic fraction was the predominant fraction in Sedalia water and it contained about 55% (3.86/6.99) of the total DOC in the filtered water sample and made a 55%/45% hydrophobic/hydrophilic separation for this water sample. The recovered transphilic fraction accounted for about 22% (1.56/6.99) of total DOC in the filtered water sample which is similar to the result previously (21%). The recovered hydrophilic fraction was about 18% (1.25/6.99) and was lower than the first water sample (20%).

Table 6.3. Fractionation of the second Sedalia Raw Water

Water Sample	DOC (mg/L)
Sedalia Raw water before filtration	6.72
Sedalia Raw water after filtration	6.99
Hydrophilic fraction	1.25
Hydrophobic fraction	3.86
Transphilic fraction	1.56
Recovered DOC (mg/L)	6.67
Fractionation Recovery (%)	95.4

Six more water samples were collected and fractionated by the same resin series system: Clarance Cannon, Jamesport, Harrison, Creighton, Higginsville, and Lexington. DOC contents of these seven surface waters fell in the range of 3.36-9.35 mg/l and DOC contents data for all the water samples as well as their isolated fractionations are shown in Table 6.4 and Figure 6.6.

Among the seven water samples, four water samples from Sedalia, Jamesport, Harrison and Creighton water plants had DOC recoveries at 98.6%, 97.7%, 102.3%, and 99.7%, respectively. These high DOC recoveries on fractionation processes indicated excellent isolation for the four samples. Samples from Clarance Cannon had a DOC recovery at 116% that was acceptable since its recovery fell into of 80%-120% which were the normal range for DOC recoveries by this isolation method (Thurman and Malcolm, 1981; Thurman, 1986). Higginsville had a recovery out of normal range of recovery (127%) and the recovery of DOC of Lexington was much higher (170%) and out of the range. The reason may be that the low DOC in raw water cause analytical variation. The millpore deionized water had a DOC value of about 0.71 mg/L and was used in the dilution procedure.

Of all the seven water samples, the hydrophobic (HPO) fraction was the predominant fraction of the DOC contents. The DOC contents of hydrophobic fraction ranged from 2.48 mg/L (Lexington) to 5.99 mg/L (Clarance Cannon) which accounted for from 43.5% (Lexington) to 58.6% (Sedalia) of the total recovered DOC. Considering the general proportion of hydrophobic fraction is 30%-50%, humic substances (fulvic acid and humic acid) level in these water samples were high.

The DOC of hydrophilic (HPI) fractions varied from 1.64 mg/L (Creighton) to 3.06 mg/L (Clarance Cannon) and accounted for about 20% (Sedalia) to 38% (Lexington) of the

total DOC. Most of the proportions of this fraction in water samples were around 25% which were similar to most other natural waters. For water sample from Lexington, this fraction was higher than 30% which was general proportion of hydrophilic fraction in most natural waters (Thurman, 1985).

The DOC contents of transphilic (TPI) fractions were ranged from 1.08 mg/L (Lexington) to 1.84 mg/L (Sedalia) and accounted for the total recovered DOC from 16.5% (Clarance Cannon) to 24.6% (Creighton). The proportion for this fraction was similar to the published data with a general range of 7% to 25% (Thurman, 1985).

The raw water samples as well as the three isolated fractions obtained were then reacted with monochloramine to study the NDMA formation and formation potential. This technique improved the fundamental understanding of the nature and behavior of natural organic material in water and their effect on NDMA formation. However, water experiencing extreme pH changes may have potential alterations in their NOM structures. Hence it is noted that the collective behavior of the individual fractions may not be the same as the behavior of the raw water sample.

Table 6.4. DOC data and fractionation recoveries of water samples

and isolated fractions

Water Sample	DOC (mg/L)	HPI		HPO		TPI		Recovered	
		DOC (mg/L)	%	DOC (mg/L)	%	DOC (mg/L)	%	DOC (mg/L)	%
Sedalia	8.71	1.72	20.0	5.03	58.6	1.84	21.4	8.59	98.6
Clarance Canon	9.35	3.06	28.2	5.99	55.2	1.79	16.5	10.85	116.0
Jamesport	7.49	1.89	25.8	4.09	55.9	1.34	18.3	7.32	97.7
Harrison	6.66	1.65	24.2	3.75	55.1	1.41	20.7	6.81	102.3
Creighton	6.56	1.64	25.1	3.29	50.3	1.61	24.6	6.54	99.7
Higginsville	5.12	1.94	29.8	3.11	47.8	1.45	22.3	6.50	126.9
Lexington	3.36	2.14	37.5	2.48	43.5	1.08	18.9	5.70	169.6
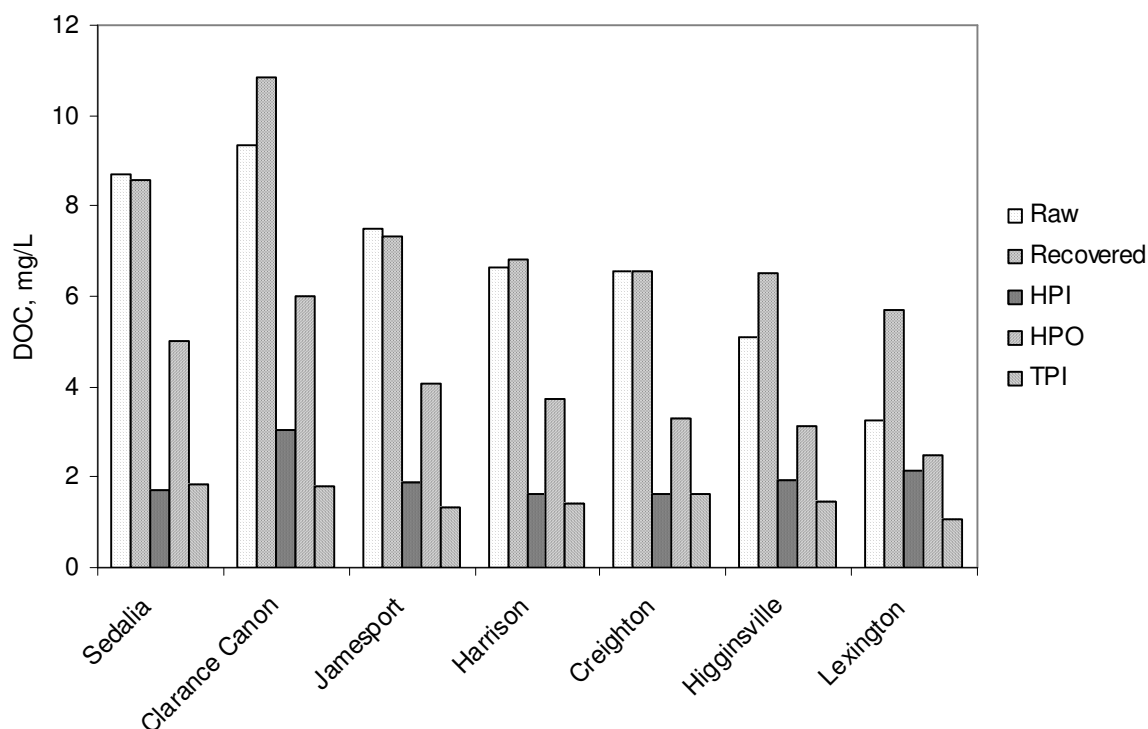
Figure 6.6. Fractionation results on 7 raw water samples in Missouri

HPI: hydrophilic fraction; HPO: hydrophobic fraction; TPI: transphilic fraction;

Recovered: the sum of three fractions

6.6   NDMA formation in raw and isolated fraction waters

After fractionation, raw water samples and fractions were adjusted to pH 8.0 by phosphate buffer solution. 500 mL of solutions for each sample (raw water and isolated fraction samples) were placed in a 1-L amber bottle with addition of calculated amount of freshly made 1 mM monochloramine stock solutions and reacted under room temperature in the dark for two days (48 hours). The formed NDMA concentrations for each sample as well as the residual monochloramine concentration are presented in Table 6.5 and Figure 6.7.

The residual monochloramine concentrations listed in the table for all samples after two days of NDMA formation reaction ranged from 0.45 mM to 0.68 mM. The monochloarmine losses during the two days were from 0.32 mM to 0.55 mM and the data showed that the monochloramine losses during the NDMA formation potential experiments had limited relationship with NDMA formation levels. This fact suggested that the monochloramine losses were caused not only by the reaction with NDMA precursor in natural waters but also by autodecomposition. However, the existing of sufficient level of monochloramine assured the available NDMA precursors could react with monochloramine completely during the reaction times and the reaction rates were not affected by the oxidant.

Table 6.5. NDMA formed concentrations and remaining monochloramine concentrations in water samples after 48 hours under pH 8.0

Water Sample	Raw		Hydrophilic (HPI)		Hydrophobic (HPO)		Transphilic (TPI)		Sum of NDMA from fractions
	NDMA, ng/L	NH2Cl, mM	NDMA, ng/L	NH2Cl, mM	NDMA, ng/L	NH2Cl, mM	NDMA, ng/L	NH2Cl, mM	
Sedalia	117	0.58	71	0.52	29	0.62	30	0.61	130
Clarance Canon	102	0.56	98	0.49	61	0.59	50	0.58	209
Jamesport	20	0.57	19	0.68	6	0.45	4	0.57	29
Harrison	20	0.45	27	0.61	1	0.55	4	0.53	32
Creighton	18	0.59	10	0.56	2	0.57	4	0.56	16
Higginsville	51	0.58	68	0.66	3	0.49	8	0.60	79
Lexington	37	0.63	55	0.59	38	0.62	22	0.57	115

Note: monochloramine concentrations were the remaining concentrations.
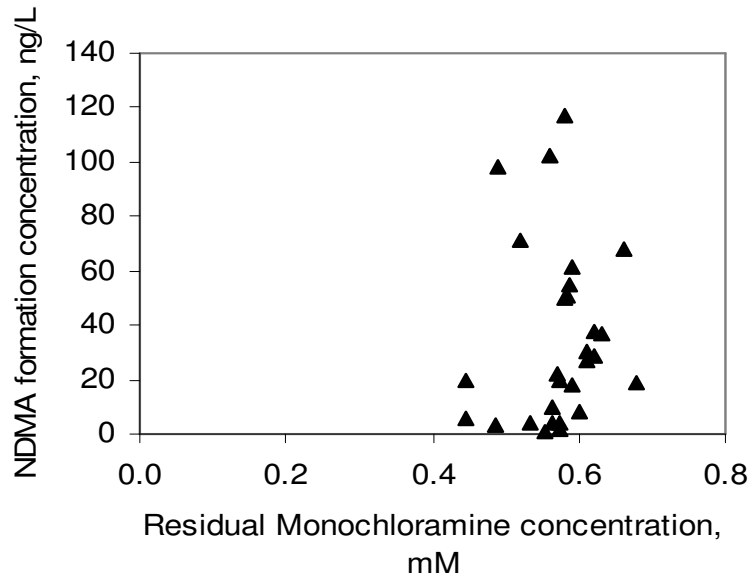
Figure 6.7. Monochloramine residual concentration and NDMA

level in all studied water samples. Monochloramine (1 mM) was

added to water samples and reacted for 2 days before the analysis

was done and water sample was adjusted to pH 8.0 by phosphate

buffer solution.
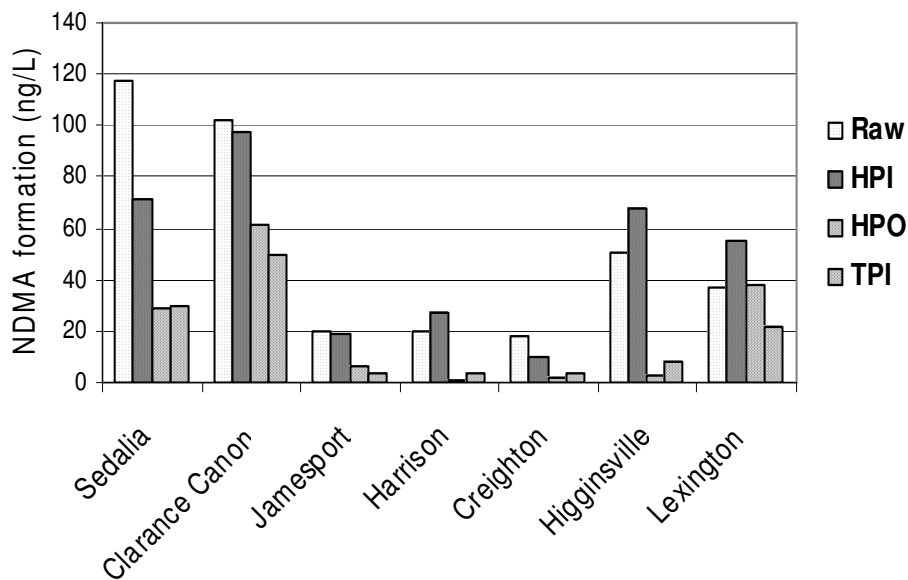
Figure 6.8. NDMA formation levels of different fractions in seven

natural waters in Missouri after reacting with 1 mM monochloramine

for 2 days. Reactions in samples were stopped by adding excess

ascorbic acid at the end of reaction and were stored in the refrigerator

until NDMA analysis.

Among all three fractions of the seven water samples, all hydrophilic fractions
yielded higher NDMA levels than the corresponding hydrophobic and transphilic fractions.
The highest NDMA formed from hydrophilic fraction was 98 ng/L from Clarance Cannon
raw water. The NDMA yields from the other two fractions from the same raw water were at
similar level (61 ng/L for the hydrophobic fraction and 50 ng/L for the transphilic fraction).
The combination of NDMA levels from hydrophilic and transphilic fractions accounted for
about 71% of the total NDMA levels formed in the three fractions.

Same situation occurred for Sedalia water sample: the hydrophilic fraction had the highest level of NDMA formation level of 71 ng/L while the hydrophobic and the transphilic fractions yielded 29 and 30 ng/L respectively. The hydrophilic fraction in Sedalia water sample yielded about 77% of the total NDMA levels formed from the three isolated fractions.

This indicated that all of the three fractions in these two water samples had the ability to produce NDMA under the conditions of high level of monochloramine oxidant. This formation capacity for the two water samples is listed in the order of:

hydrophilic fraction > hydrophobic fraction ≥ transphilic fraction

This order of the NDMA formation ability was also formed for other water samples as Jamesport and Lexington. For water samples from Harrison and Creighton, NDMA levels from their hydrophobic and transphilic fractions were low and could be ignored.

When the total formed NDMA concentrations from three fractions were compared to NDMA from raw waters, all samples were found much higher than their corresponding raw water except Creighton which had similar data for both results. This phenomenon may be explained as follows: The water samples experienced extreme pH changes during the isolation fractions process since water samples were adjusted to pH 2.0 by sulfuric acid and hydrophobic and transphilic fractions were washed by 1.0 N NaOH solution and pH could reach up to 12.5. These changes may have altered certain structures of the NOM and affected their original chemical properties. Moreover, the interactions among structures may have affected the NDMA precursors' reactivity in water. However, the results still provide information on understanding the relative NDMA formation in different fractions in natural waters.

As the linear relationships between formed NDMA yields and DOC in the raw water and separated fractions were studied, it was found that hydrophilic fraction had a closer relationship to DOC than raw water or the other two fractions. As shown in Figure 6.9, the R^2 for linearity between NDMA yield and DOC contents in the raw, hydrophobic, and transphilic fractions in these 7 water samples were 0.33, 0.32, 0.25, while that for hydrophilic fraction was 0.54. The results suggested that the hydrophilic fraction contained chemicals or structures that contributed more to form NDMA in the natural waters.
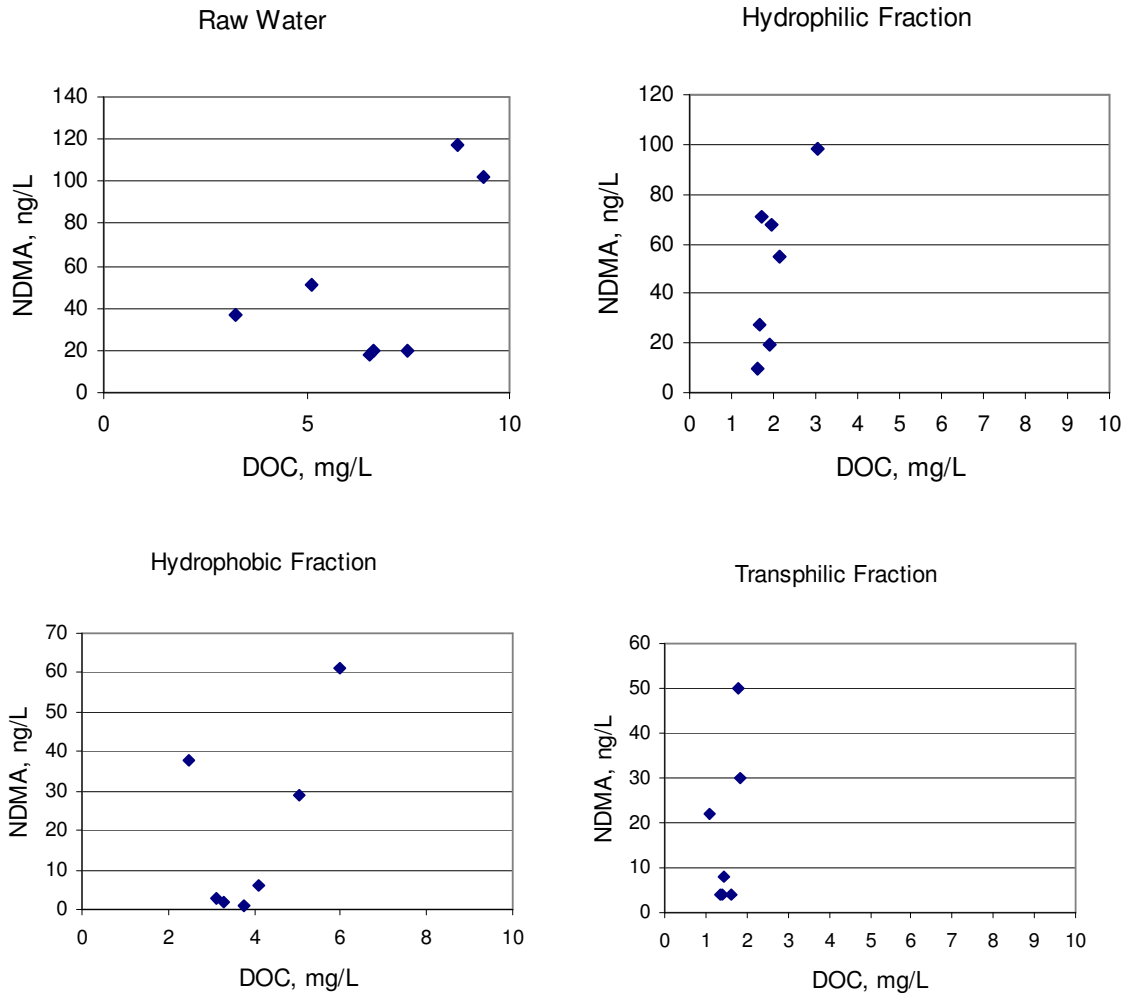
Figure 6.9. NDMA yields versus DOC contents in the origin and isolated surface water samples. All samples reacted with 1 mM monochloramine for 2 days.

6.7   NDMA formation potentials in water samples

The NDMA formation potential was determined as the NDMA precursors divided by the DOC concentration of the solution. It is expressed in unit of ng NDMA/mg C. The value of the parameter indicates the ability of the solution to form NDMA (Table 6.6 and Figure 6.10).

In Sedalia water sample, the NDMA formation potential of the hydrophilic fraction was 41.3 ng/mg C which meant NDMA production concentration was 41.3 ng/L with 1 mg/L DOC content in raw water. For the hydrophobic fraction this value was 5.8 ng/mg C which was only 14% of the hydrophilic fraction's production. Among all the samples, NDMA precursors from hydrophilic fractions varied from 6.1 to 41.3 ng NDMA/mg C, four out of seven have the value higher than 25 ng/mgC. For the hydrophobic fractions, the values drop dramatically, which varied between 0.27-15.3 ng/mgC, and four of them are very low (below 1.5 ng/mgC). The values for transphilic fractions also vary. Three of them are higher than 16 ng/mgC while four of them are about 3 ng/mgC. It is obvious that hydrophilic fractions have the largest NDMA formation potentials among the three fractions while hydrophobic fractions have the least. Considering the percentages of three fractions in the sum of NDMA formation potentials of three fractions, the hydrophilic fraction accounts for the highest among the three for all the water samples (41.9% to 84.4%) and five out of seven have the percentage over 65%. While for the hydrophobic and transphilic fractions, the percentages fall in 1.4-25%, and 13-40% respectively.

Table 6.6. NDMA Formation Potential (NDMAFP) of raw and three fractions in 7 studied water samples

	Parameters	Sedalia	Clarance Canon	Jamesport	Harrison	Creighton	Higginsville	Lexington
Raw	DOC, mg/L	8.71	9.35	7.49	6.66	6.56	5.12	3.26
	NDMA, ng/L	117	102	20	20	18	51	37
	NDMAFP, ng/mg C	13.4	10.9	2.7	3.0	2.7	10.0	11.3
HPI	DOC, mg/L	1.72	3.06	1.89	1.65	1.64	1.94	2.14
	NDMA, ng/L	71	98	19	27	10	68	55
	NDMAFP, ng/mg C	41.3	32.0	10.1	16.4	6.1	35.1	25.7
HPO	DOC, mg/L	5.03	5.99	4.09	3.75	3.29	3.11	2.48
	NDMA, ng/L	29	61	6	1	2	3	38
	NDMAFP, ng/mg C	5.8	10.2	1.5	0.27	0.61	1.0	15.3
TPI	DOC, mg/L	1.84	1.79	1.34	1.41	1.61	1.45	1.08
	NDMA, ng/L	30	50	4	4	4	8	22
	NDMAFP, ng/mg C	16.3	27.9	3.0	2.8	2.5	5.5	20.4
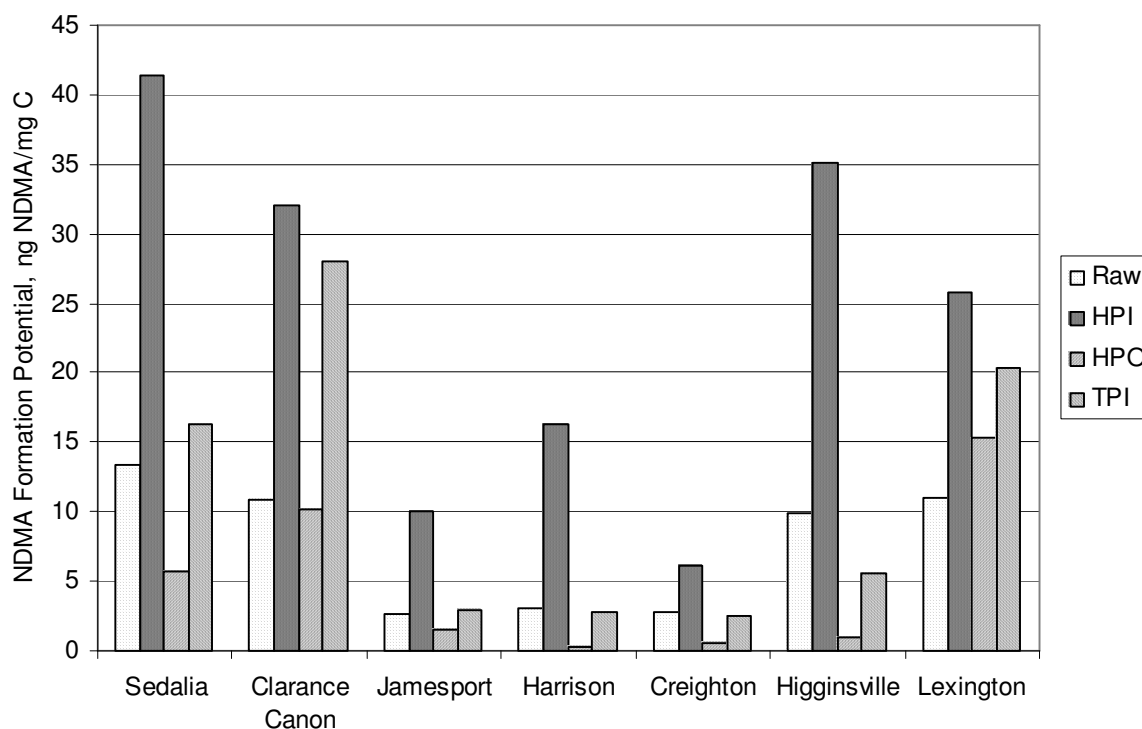
Figure 6.10. NDMA formation potential (NDMAFP) in raw and three fractions in seven

natural waters

6.8   Kinetic study of NDMA formation in natural water

Raw water and three fractions of Sedalia water reacted with 1 mM monochloramine

for 0.5, 6, 10, 24, 48, 120, and 168 hours. For each sample, the monochloramine

concentration was measured first, and ascorbic acid was then added to quench the

monochloramine in the water sample. Concentration data of residual monochloramine and

NDMA in solutions when reactions were ceased are listed in Table 6.7 and Figure 6.11.

Residual monochloramine concentration in four reacted waters did not differ much

after 24 hours contact with NDMA precursors in fractionated and raw water samples even

though the amount of formed NDMA differed greatly in raw water and three fractions. After

that, the monochloramine losses increased with both reaction time and NDMA formation levels.

The NDMA formation level for the raw water increased dramatically during the first 24 hours. From the second day to the fifth day, its formation rate decreased until it reached the maximum concentration on the fifth day. This suggested the NDMA precursors were consumed after contact with the high concentration of monochloramine for five days. The hydrophobic fraction had similar situation on its formation rate however the concentration was 70% lower.

The hydrophilic fraction and transphilic fraction were different. Like the other two samples mentioned above, the formation rates for these two fractions were fast on the first two days and then decreased the next three days. However, unlike the previous fractions, the NDMA formation of these two fractions did not stop but still increased.

It is possible that the precursors in hydrophilic fractions were not consumed and with sufficient monochloramine available, it still produced NDMA. Since there was overlap between fractions which shared similar characteristics during the separation process, it was reasonable that transphilic fraction had the same increase trend in the transphilic fraction. Because the hydrophilic fraction only accounted for a small amount of DOC contents in raw water, NDMA formation from precursors in hydrophilic fraction was not large in raw water.

Table 6.7. Data of NDMA formation kinetic study on Sedalia raw water and three fraction

waters

Reaction	RAW		HPI		HPO		TPI	
Time	NH2Cl	NDMA	NH2Cl	NDMA	NH2Cl	NDMA	NH2Cl	NDMA
(hr)	mM	ng/L	mM	ng/L	mM	ng/L	mM	ng/L
0.5	1.00	0	0.93	0	0.99	0	1.00	0
6	0.88	36	0.92	6	0.92	5	0.91	3
10	0.88	60	0.91	22	0.90	8	0.88	6
24	0.80	104	0.84	38	0.81	20	0.80	21
48	0.48	112	0.52	65	0.62	24	0.61	24
120	0.37	132	0.39	81	0.52	37	0.48	40
168	0.32	133	0.35	99	0.48	38	0.44	56
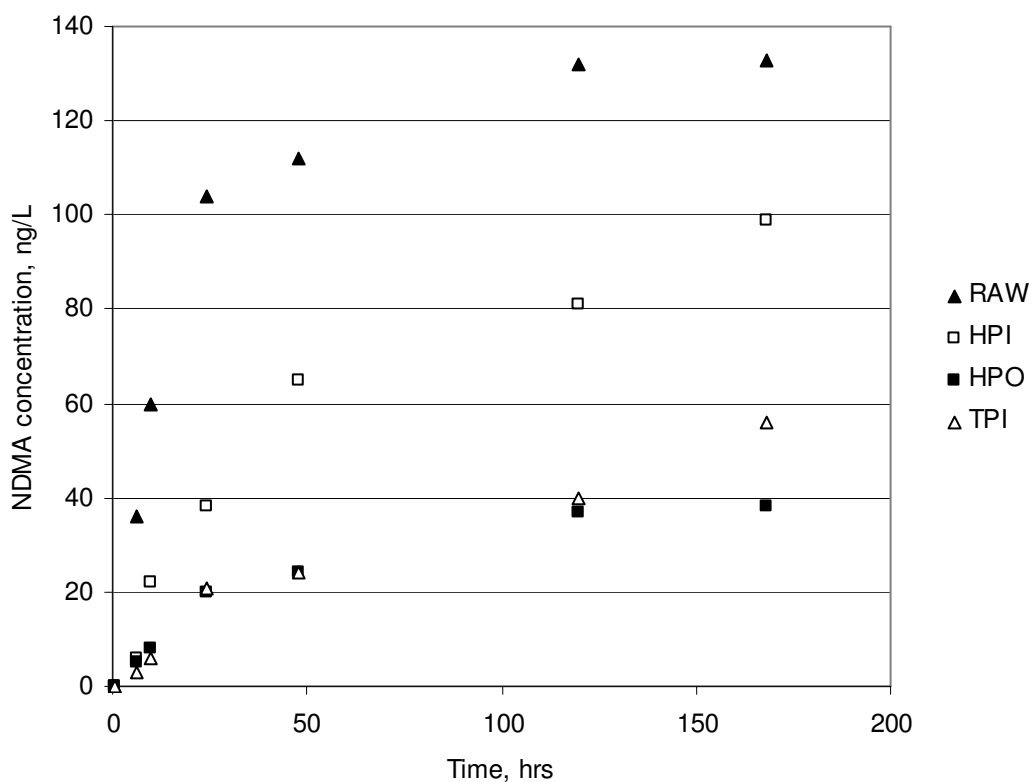
Figure 6.11. Kinetic study of NDMA formation on Sedalia Raw Water and
three fractions water samples. Monochloramine of 1 mM was added to
each water sample and reacted for up to 168 hours. Reactions were
conducted under room temperature and pH 8.0.

6.9   Effect of pH on the formation study of different fractions in natural water

         After fractionation process, Sedalia water sample pHs were adjusted with
concentrated sulfuric acid and NaOH solutions to the range from 6.0 to 9.0. Phosphate buffer
solution (10 mM) was applied to augment buffer capacity of the water samples.

         As shown in Table 6.8 and Figure 6.12, the NDMA formation potential increased as
pH increased in raw water, hydrophilic fraction, and hydrophobic fraction, especially for

hydrophilic fraction. This was not unexpected because monochloramine autodecomposition

was acid-catalyzed and monochloramine losses increased as pH decreased. Hydrolysis of

monochloramine is a reaction pathway that produces HOCl which reacts with additional

monochloramine to form dichloramine as shown in Eqn. 2.2 and Eqn. 2.3.

$$NH_2Cl + H_2O \Leftrightarrow NH_3 + HOCl \qquad \text{Eqn. 2.2}$$

$$NH_2Cl + HOCl \rightarrow NHCl_2 + H_2O \qquad \text{Eqn. 2.3}$$
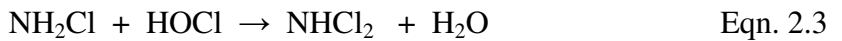
Another pathway for monochloramine disproportionation is that monochloramine is

catalyzed by hydrogen ion according to the Eqn. 6.1 and Eqn. 6.2 (Granstrom, 1954; Morris,

1967; Gray et al., 1978; Valentine and Jafvert, 1988).

$$NH_2Cl + H^+ \Leftrightarrow NH_3Cl^+ (+ A^-) \qquad \text{Eqn. 6.1}$$

$$NH_3Cl^+ + NH_2Cl \rightarrow NHCl_2 + NH_3 + H^+ \qquad \text{Eqn. 6.2}$$
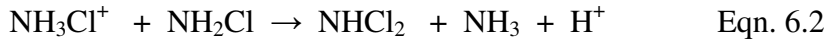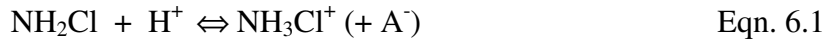
Table 6.8. Data of NDMA and NDMA Formation Potential in

Sedalia raw water and three fraction waters under variable pH

conditions

pH	RAW		HPI		HPO		TPI	
	NDMA ng/L	NDMAFP ng/mg C	NDMA ng/L	NDMAFP ng/mg C	NDMA ng/L	NDMAFP ng/mg C	NDMA ng/L	NDMAFP ng/mg C
6	27	3.1	28	16.3	19	3.8	37	20.1
7	81	9.3	27	15.7	25	5.0	28	15.2
8	117	13.4	71	41.3	29	5.8	30	16.3
9	211	24.2	88	51.2	68	13.5	32	17.4
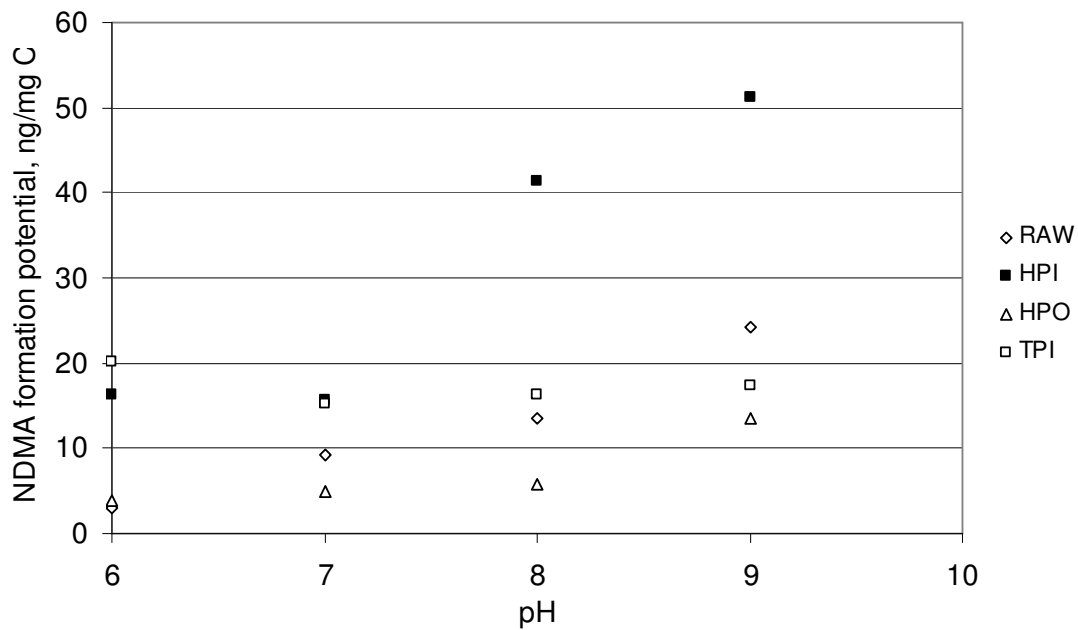
Figure 6.12. pH effect on NDMA formation potential in

Sedalia raw water and three fraction waters. Monochloramine

with 1 mM concentration was added and reacted for 48 hours.

pH was adjusted by sulfate acid and sodium hydroxyl and

buffered with phosphate buffer solution.

6.10   Summary

Monochloramine decomposed at high concentration levels and the concentration of stock solutions had to be checked before application. Even at low concentration, it decomposed at a lower rate and trace levels of NDMA were produced in DIUF water. Results showed that sedimentation could remove a part of NDMA precursors in Sedalia water samples.

Isolation of seven water samples showed that hydrophobic fractions were the predominant fraction while hydrophilic fraction could produce the most NDMA in its isolated state. The NDMA formation potential (NDMAFP) for each fractions was expressed in ng NDMA/mg C and it was an indicator of the NDMA production ability of each sample. NDMAFP was highest in hydrophilic fraction and lowest in hydrophobic fraction in all studied seven water samples. NDMAFP increased greatly with pH, changes greatly improved reactivity of NDMA precursors in isolated fractions.

CHAPTER 7

ROLE OF BROMIDE ION IN NDMA FORMATION

IN NATURAL WATERS

7.1   Introduction

Bromide ion is a common component in most drinking water and wastewater and its concentration varies with different water sources. It was reported to affect the formation of disinfection by-products (Shukairy et al., 1995). Monochloramine is usually applied by adding chlorine as chlorine gas or hypochlorite solution and ammonia/ammonium salt to water or to water with ammonia. The added chlorine rapidly hydrolyses to HOCl and OCl⁻ in water. Ammonium (Margerum et al., 1978) and bromide (Bousher et al., 1986) existing in the water reacts rapidly with hypochlorous acid (Eqn. 7.1 and Eqn. 7.2). The rates of both reactions are pH dependent and the overall yield of these two competitive reactions depends on the relative concentrations of bromide and ammonia.

$$HOCl \ + \ NH_3 \ \rightarrow \ NH_2Cl \ + \ H_2O \qquad\qquad \text{Eqn. 7.1}$$

$$HOCl \ + \ Br^- \ \rightarrow \ HOBr + \ Cl^- \qquad\qquad \text{Eqn. 7.2}$$
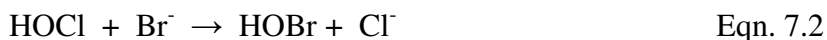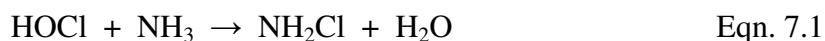
Hypochlorous acid does not react with the ammonium ion. Under a moderate high pH up to 8, equilibrium between ammonia and ammounium ion is more favorable for ammonia. So with a moderate high pH and low bromide ion concentration, monochloramine production is more pronounced than hypobromous acid.

118

The HOBr formed could then react with the ammonia as shown in Eqn. 7.3 just like the production of monochloramine in Eqn. 2.2.

$$NH_3 \ + \ HOBr \ \rightarrow \ NH_2Br \ + \ H_2O \qquad\qquad \text{Eqn. 7.3}$$
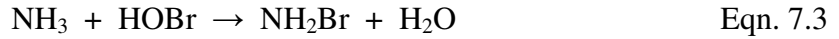
Bromide ion can be oxidized by monochlormaine through NH_3Cl^+ formation. The following reaction scheme was proposed by Trofe et al. (1980).

$$NH_2Cl \ + \ H^+ \ \leftrightarrow \ NH_3Cl^+ \qquad\qquad \text{Eqn. 7.4}$$

$$NH_3Cl^+ \ + \ Br^- \ \rightarrow \ NH_3Br^+ \ + \ Cl^- \qquad\qquad \text{Eqn. 7.5}$$

$$NH_3Br^+ \ + \ NH_2Cl \rightarrow \ NHClBr \ + \ NH_4^+ \qquad\qquad \text{Eqn. 7.6}$$
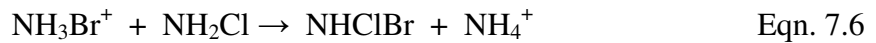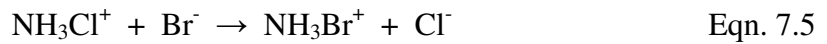
The use of chloramines rather than chlorine as a primary disinfectant avoids reactions of ammounium oxidation by free chlorine and could more focus on chloramine/bromide reactions, especially as fresh waters may be much less well-buffered than sea and estuarine waters.

Monobromamine is expected to react with DMA in a manner analogous to monochloramine to produce NDMA and the increased negative charge of the brominated nitrogen of monobromanine is expected to increase the rate of UDMH formation with monobromamine (Choi, 2002c). The increase could be achieved by two pathways: the oxidation of bromide by monochloramine, and the production of HOBr from oxidation of bromide by HOCl which reacts with ammonia to form bromamines. Since the oxidation of

bromide by monochloramine is slow, the increase in NDMA formation from the first

pathway is slow.

7.2   Effect of bromide concentration on NDMA formation

Water samples from Sedalia were collected, filtered, and adjusted to pH 7.0 with

sulfuric acid. To study the effect of bromide ion concentration on NDMA formation,

potassium bromide solution was added to the water samples to make the bromide ion

concentrations of 0, 0.1, 0.2, 0.5, 1, and 2 mM, respectively. Prepared monochloramine stock

solution was added to make the monochloramine concentration of 1 mM in water samples

and reacted for 48 hours. The results of NDMA formation are shown in Figure 7.1.

With increasing bromide ion concentration in the water, NDMA formation after 48

hours increased. However, while the concentration of bromide ion varied from 0 to 2 mM,

the increase of NDMA formation in Sedalia raw water was only 6 ng/L (changed from 23 to

29 ng/L) which was small. The result indicated that the precursor in the raw water was

limited and bromide had limited effect on NDMA formation.

Table 7.1. Data on NDMA formation in Sedalia raw water with 1 mM monochloramine and

variable bromide concentrations (pH was adjusted to 7.0 and reacted for 48 hours)

| Concentration of Br- (mM)	0	0.1	0.2	0.5	1	2
Monochloramine (mM)	0.52	0.40	0.28	0.12	ND	ND
NDMA formation (ng/L)	23	21	24	25	27	29

Note: ND refers to not detected.
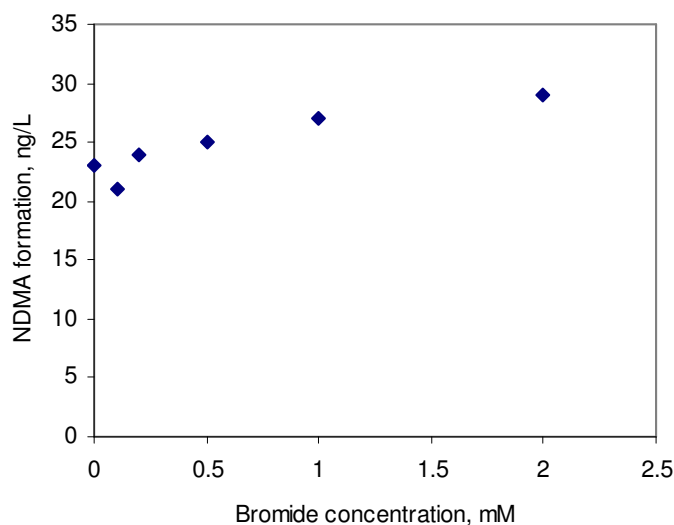
Figure 7.1. NDMA formation in Sedalia raw water in the presence of

preformed monochloramine and variable bromide concentrations in water.

Reaction lasted for 48 hours and was adjusted to pH 7.0 with sulfate acid

and buffered with 4 mM sodium bicarbonate.

Since most utilities use the addition of free chlorine and ammonium salt instead of preformed monochloramine, the effect of bromide ion to NDMA formation in the system of ammonium chloride and sodium hypochlorite was also studied. It can be seen from the data in Table 7.2 and Figure 7.2, the NDMA formation in the system was much lower than that from the system with prepared monochloramine as the disinfectant. This may be related to the low concentration of monochloramine produced through the separate addition of ammonium chloride and sodium hypochlorite.

Although there was low NDMA yield in this system, a maximum of NDMA formation was present at the concentration of 0.1 mM for bromide ion. As bromide ion concentration increased above 0.1 mM, NDMA yield decreased until almost disappeared. These results were similar to the result from DMC reaction with hypochlorous acid and ammonium except the concentration of NDMA was much lower (Choi, 2002C). It is reasonable to have lower NDMA yield because whatever precursors exists in the Sedalia water, their concentration is much lower than the DMC concentration applied in the lab. The maximum NDMA yield in the system by adding hypochlorous acid and ammonium salt separately could be explained by bromide ion accelerated NDMA formation and oxidation of monochloramine or hypochlorite as well. At the low level of bromide, NDMA formation increases as oxidant is available. As bromide ion concentration increases, it also consumes oxidant for NDMA and thus the reaction stops.

Table 7.2. Data on NDMA formation in Sedalia raw water with 1.2 mM ammonium, 1 mM

sodium hypochlorite and variable bromide concentrations (pH was adjusted to 7.0 and

reacted for 48 hours)

Concentration of Br- (mM)	0	0.1	0.2	0.5	1
Monochloramine (mM)	0.15	0.08	0.04	ND	ND
NDMA formation (ng/L)	9	12	8	6	4

Note: ND refers to not detected.
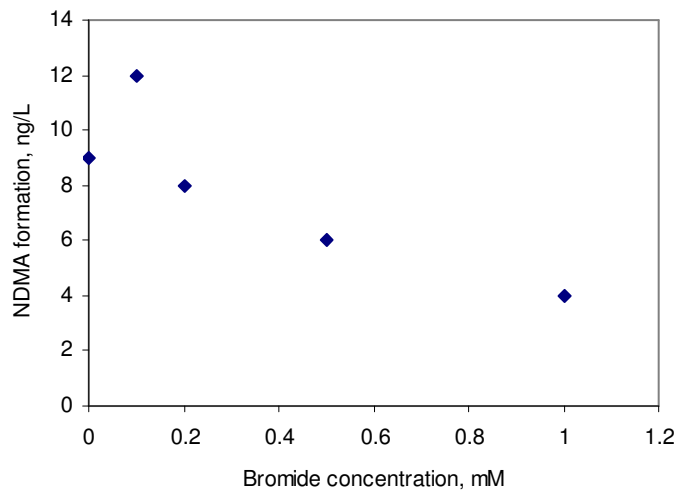
Figure 7.2. NDMA formation in Sedalia raw water in the presence of

1.2 mM ammonium chloride, 1 mM sodium hypochlorite, and variable bromide

concentrations in water. Reaction lasted for 48 hours and was adjusted

to pH 7.0 with sulfate acid and buffered with 4 mM sodium bicarbonate.

Same experiment was conducted on the hydrophilic fraction of Sedalia water (Figure 7.3) and Clarance Cannon raw water (Figure 7.4)., NDMA formation levels in these two water samples were higher than those in Sedalia raw water samples indicating that NDMA precursors were higher in these two samples. As bromide ion concentration increased, the formed NDMA levels also increased. Furthermore, in the water samples with higher precursors, the accelerating effect of bromide was more obvious.
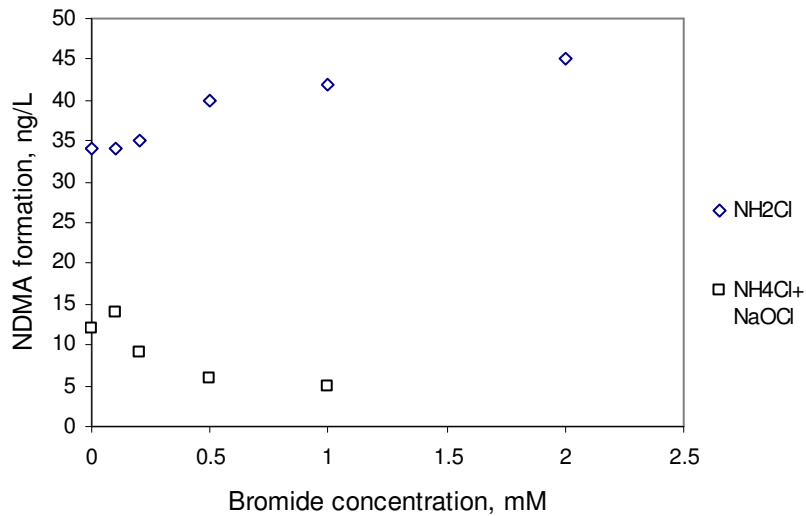
Figure 7.3. NDMA formation in Sedalia hydrophilic fraction water in the presence of ○: 1 mM preformed monochloramine; and □: 1.2 mM ammonium chloride, 1 mM sodium hypochlorite; and variable bromide concentrations in water. Reaction lasted for 48 hours and was adjusted to pH 7.0 with sulfate acid and buffered with 4 mM sodium bicarbonate.
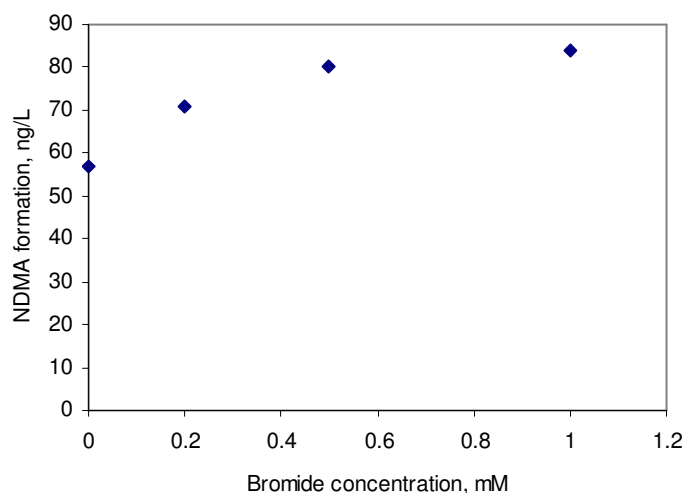
Figure 7.4. NDMA formation in Clarance Cannon raw water in the presence of

preformed monochloramine and variable bromide concentrations in water.

Reaction lasted for 48 hours and was adjusted to pH 7.0 with sulfate acid

and buffered with 4 mM sodium bicarbonate.

7.3   Effect of pH on NDMA formation with bromide ion present

The effect of pH on NDMA formation was studied in Sedalia hydrophilic fraction

with and without bromide ion present. PH ranged from 6.0 to 9.0 and data in Figure 7.8

showed that pH effect on NDMA formation with 0.5 mM bromide ion was very profound. As

pH increased, NDMA formation increased in water both with bromide ion and without

bromide ion. With bromide ion present, NDMA levels increase greatly especially at pH 9.0.

This may be explained by the acid dependency of bromamine formation from bromide

oxidation by monochloramine. As pH increases, bromamine formation rate decreases and its

stability increases, resulting in complete reaction with NDMA precursors.
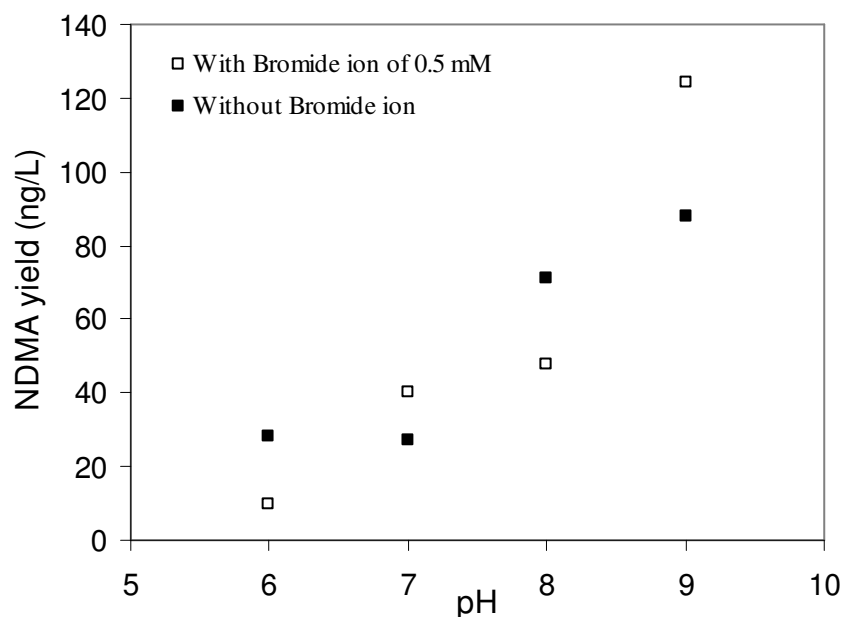
Figure 7.5. NDMA formation in Sedalia hydrophilic fraction water

□: with 0.5 mM bromide ion present; ■: without bromide ion present;

at various pH (6, 7, 8, and 9) using 1 mM preformed monochloramine.

Reaction lasted for 48 hours and pH was adjusted by sulfate acid

and buffered with 4 mM sodium bicarbonate.

7.4   Summary

Bromide ion was studied for its role in NDMA formation in natural water samples. It was found that it could slightly accelerate NDMA formation in chloraminated and chlorinated water containing ammonium at low bromide ion concentration. Effect of pH on the NDMA formation with presence of bromide ion was studied and NDMA formation was accelerated with increasing pH and was more distinct in natural water with presence of bromide ion than without bromide ion.

CHAPTER 8

CONCLUSIONS AND RECOMMENDATIONS

8.1   Conclusions

The analytical methods for the analysis of N-nitrosodimethylamine (NDMA) in drinking water samples for measurement in the part per trillion ranges were developed. The Liquid-liquid extraction (LLE) method and Solid phase extraction (SPE) method were applied in the extraction procedure coupled with ion trap mass spectrometer (MS) with chemical ionization (CI) in the mode of selected ion storage (SIS). Analysis results from two extraction methods were compared and evaluated. Solid phase extraction with GC/MS/CI/SIS instrument analysis method presented a reliable, accurate, practical, and cost-effective procedure for the routine analysis of NDMA at a trace level in drinking water samples.

The developed analysis method was applied in the analysis of NDMA in ten drinking water utilities in Missouri which used monochloramine as a primary disinfectant, four utilities were found to have NDMA higher than the 10 ng/L action level set by California Department of Health and Services. The detected NDMA levels in these utilities indicated that DOC played an important role in the NDMA formation in natural waters.

Isolation of natural organic matter (NOM) in seven water samples in Missouri showed that hydrophobic fractions were the predominant fraction while hydrophilic fraction produced the most NDMA in its isolated state. The NDMA formation potential (NDMAFP) for each fractions was expressed in ng NDMA/mg C and it was an indicator of the NDMA production ability of each sample. NDMAFP was the highest in hydrophilic fraction and

lowest in hydrophobic fraction in all studied seven water samples. An evident influence was found in NDMAFP that increased pH greatly improved reactivity of NDMA precursors in isolated fractions and raw water in Sedalia water sample, especially in hydrophilic fraction.

Bromide ion was studied for its role in NDMA formation in natural water samples. It was found that it could slightly accelerate NDMA formation in chloraminated and chlorinated water containing ammonium at low bromide ion concentration. Effect of pH on the NDMA formation with presence of bromide ion was studied and results showed that increased NDMA formation with increasing pH was more distinct in natural water with the presence of bromide ion than without bromide ion.

The findings reported in this dissertation provide data on NDMA occurrences in drinking water and natural waters in Missouri. The results explain reasonable and practical source of NDMA precursors in natural waters and this information could be used in the further study of mitigating NDMA formation or removing NDMA precursors in drinking water utilities. The results on factors affecting on NDMA formation provides more information for water utilities to determine operation conditions to reduce and control NDMA formation in water treatments.

8.2   Recommendations

The study results in the NDMA formation study showed that not only are chloramination conditions important in NDMA formation in natural waters, but also the origin and nature of the NOM plays an important role. A future study on the relationship between the chemical structure and NDMA formation potentials of NOM fractions is recommended. The application of the techniques of high-resolution solid-state nuclear magnetic resonance (NMR) spectroscopy and pyrolysis gas chromatography-mass spectrometry has improved our understanding of the structure of aquatic organic matter (Hayes, et al.; Saiz-Jimenez, 1989). Using the methods provided by Hanna (Hanna, et al., 1991), 8 and 18 structures could be determined by applying ^{13}C NMR and pyrolysis GC/MS, respectively.

BIBLIOGRAPHY

Aiken, G.R.; McKnight, D.M., et al. (1992). Isolation of hydrophilic organic acids from water using nonionic macroporous resins. *Org. Geochem.* 1992. 18(4), 567-573

American Water Works Association, American Society of Civil Engineers (1997). Water Treatment plant design (3rd Edition). McGraw-Hill Companies, Inc. ISBN 0-07-001643-7.

Andrews, S.A. and Taguchi, V.Y. (2000). NDMA-Canadian Issues. *American Water Works Association, Water Quality Technology Conference Proceedings*. Salt Lake City, UT; 2000, Nov.

ASTDR. http://www.atsdr.cdc.gov/toxprofiles/tp141-c3.pdf (accessed Sept. 2005)

Ayanaba, A.; and Alexander, M. (1974). Transformations methylamines and formation of a hazardous product, dimethylnitrosamine, in samples of treated sewage and lake water. *J. Environ. Qual.* 3(1), 83-89

Banerjee, S.; Pack, E.J.; Sikka, H.; and Kelly, C.M. (1984). Kinetics of oxidation of methylhydrazines in water. Factors controlling the formation of 1,1-dimethylnitrosamine. Chemosphere 13(4), 549-559

Barrett, Sylvia; Hwang, Cordelia; et al. (2003). Occurrence of NDMA in Drinking Water: A north American Survey, 2001-2002. Amercian Water Works Association Annual Conference.

Berger, R.; Hunsinger, R.; Sykes, C.; Smith, J.; Sheikolasami, A.; Wilczek, A.; and Lai, H. (2002). An approach for responding to emerging contaminants: East Bay Municipal District's experience with NDMA. In *Proceedings of Annual AWWA Conference*. New Orleans.

Bongers, L.H.; O'Connor, T.P.; Barton, D.T. (1977). U.S.Environmental Protection Agency, Report No. EPA-600/7-77-053.

Bousher, A.; Brimblecombe, P. and Midgley, D. (1986). Rate of Hypobromite Formation in Chlorinated Seawater. *Water Research*. 20(7), 865-870

Bousher, A.; Brimblecombe, P., and Midgley, D. (1989). Kinetics of reactions in solutions containing monochloramine and bromide. Water Research. 23(8), 1049-1058

Brewer, W.S.; Draper, A.C., et al. (1980). The detection of dimethylnitrosamine and diethylnitrosamine in municipal sewage sludge applied to agricultural soils. *Environ. Pollut., Ser. B: Chem. Phys*. 1(1), 37-43

Brooks, J.B., Cherry, W.B., Thacker, L., Alley, C.C. (1972). Analysis by gas chromatography of amines and nitrosamines produced in vivo and in vitro by Proteus vulgaris. *J. Infec. Dis.* 126, 143

California Cancer Potency Values (2002). http://www.oehha.ca.gov/risk/pdf/Cancer%20potency%20list%20May2002.pdf (accessed Sept. 2005)

Castegnaro, M.; Brouet, I.; Michelon, J.; Lunn, G.; and Snsone, E.B. (1986). Oxidative destruction of hydrazines produces N-nitrosamines and other mutagenic species. *Am. Ind. Hyg. Assoc. J.* 47, 360-364

Cerutti, A.D. and Airoldi, L. (1996). Volatile N-Nitrosamines in Selected Italian Cheeses. Environmental Contamination and Toxicology, 57, 16-21

CDHS, California Department of Health and Safety. http://www.dhs.ca.gov/ps/ddwem/chemicals/NDMA/history.htm (accessed Sept. 2006)

Chapin, R. M. (1931). *J. Amer. Chem. Soc.*, 53, 912

Challis, B.C.; Kyrtopoulos, S.A. (1979). *J. Chem. Soc., Perkin Trans. 1*, 299-304

Choi, J.H. and Valentine, R.L. (2002a). Formation of N-nitrosodimethylamine (NDMA) from reaction of monochloramine: A new disinfection by-product. *Water Res.* 36(4), 817-824.

Choi, J.H. and Valentine, R.L. (2002b). A kinetic model of N-nitrosodimethylamine (NDMA) formation during water chlorination/chloramination. *Water Sci. Technol.* 46(3), 65-71.

Choi, J.H. (2002c). Mechanistic studies of N-Nitrosodimethylamine (NDMA) in Model Drinking waters. Ph.D. Dissertation.

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

Christman, R.F.; Norwood, D.L., et al. (1983). Identity and yields of major halogenated products of aquatic fulvic acid chlorination. *Environ. Sci. Techno.* 17(10): 625

Clark, C.C. (1953). Hydrazine, 1st ed.; Mathieson Chemical Corp.:Baltimore, 1953.

Clesceri, L.S.; Greenberg, A.E.; Eaton, A.D., Eds. Standard Methods for the Examination of Water and Wastewater, 20th ed.. American Public Health Association, American Water Works Association, Water Environment Federation Publishers: Washington, DC, 1998

Cole, S.A.; Taylor, W.C.(1956). *Tappi*, 39, 62A

Corbett, R.E.; Metcalf, W.S.; Soper, F.G. (1953). *J. Chem. Soc.* (London), 1927

Cromwell, B.T., and M. Richardson. 1966. Studies on the biogenesis of some simple amines and quarternary ammonium compounds in higher plants. Trimethylamine in Chenopodium vulvaria L. Phytochemistry 5:735-746

Croue J.P.; Martin B.; et al. (1993). *Water Supply*. 11, 79

Croue J.P.; Violleau, D.; and Labouyrie L. (2000). Disinfection By-Product Formation Potentials of Hydrophobic and Hydrophilic Natural Organic Matter Fractions: A Comparison Between a Low- and a High-Humic Water. ACS Symposium Series (2000), 761(Natural Organic Matter and Disinfection By-Products). 139-153

Czech, F. W.; Fuchs, R.J., et al. (1961). Determination of Mono-, Di-, and Trichloramine by Ultraviolet Absorption Spectrophotmetry. Anal. Chem., 33, 705

Delalu, H.; and Marchand, A.(1987). Determination des conditions de formation de la formaldehyde dimethylhydrazine asymetrique (FDMH) par oxidation de la dimethylhydrazine asymetrique (UDMH) par la chloramines. II. Mecanisme reactionnel de formation de la FDMH formulation et modelisation. *J.Chim. Phys.* 84(9), 997-1001

Delalu, H.; and Marchand, A.(1989a). Influence d'une ionization des reactifs sur l'aspect mecanistique de l'interaction chloramines-dimethylamine. Formation parallele de dimethyl-hydrazine et de dimthylchloramine. *J.Chim. Phys.* 86(9), 1941-1953

Delalu, H.; and Marchand, A.(1989b). Modelisation generale des processus reactionnels intervenant au cours de la synthese de la dimethylhydrazine asymetrique par le procede Raschig. Wuantificatio des produits de degradation (hydrazone). J. Formulation du modele. Validite en milieu dilue. Interpretation. *J.Chim. Phys.* 86(11/12), 2149-2162

Delalu, H.; Marchand, A.; Ferriol, M.; and Cohenadad, R. (1981). Cinetique de la reaction de formation de la dimethylhydrazine asymetrique par action de la monochloramine sur la dimethylamine. *J. Chim. Phys*. 78(3), 247-252

Douglass, M.L.; Kabacoff, B.L.; Anderson, G.A.; Cheng, M.C. (1978). *J. Soc. Cosmet.Chem.* 29, 581-606

Eaton, A. and Briggs Mike. (2000). NDMA-Analytical methods options for a new disinfection byproduct. *American Water Works Association, Water Quality Technology Conference Proceedings*. Salt Lake City, UT; 2000, Nov.

Fajen, J.M.; Carson, G.A.; Rounbehler, D.P.; Fan, T.Y.; Vitae, R.; Goff, U.E.; Wolf, M.H.; Edwards, G.S.; Fine, D.H.; Reinhold, V.; Biemann, K. (1979). N-nitrosamines in the rubber and tire industry. *Science* 205(4412), 1262-4

Fan, T.Y. and Tannenbaum, S.R. (1973). Factors influencing the rate of formation of nitrosomorpholine from morpholine and nitrite: Acceleration by thiocyanate and other anions. *J. Agric. Food. Chem.* 21, 237-240

Fiddler, W.; Pensabene, J.W.; Doerr, R.C.; and Wasserman, A.E. (1972). Formation of N-nitrosodimethylamine from naturally occurring quaternary ammonium compounds and tertiary amines. *Nature* 236, 309

Fine, D.H; Ross, R.; Rounbehler D.P.; Silvergleid A.; Song L. (1977). Formation in vivo of volatile N-nitrosamines in man after ingestion of cooked bacon and spinach. *Nature* 265(5596), 753-5

Fishbein, L.; Flamm, W.G.; and Falk, H.L. (1970). *Chemical Mutagens, Environmental Effects on Biological Systems.* Academic Press, New York. 206-211

Gang, D.; Clevenger, T.E., et al. (2003). Relationship of chlorine decay and THMs Formation to NOM size. *Journal of Hazardous Materials (Elsevier Science)*, 96(1), 1-12

Gerecke, A. C. and David L. Sedlak. (2003). Precursors of N-nitrosodimethylamine in natural waters. *Environ. Sci. Technol*. 37, 1331-1336

Granstrom, L.M. Ph.D. Dissertation, Harvard University, Cambridge, MA, 1954

Gray, E.T.; Margerum, D.W.; Huffman, R.P. In Organometals and Organometaloids; Brinkman, F.F.; Bellama, J.M., Eds.; American Chemical Soceity: Washington, DC, 1978; 264-277

Greene, S.; Alexander, M.; and Leggett, D. 1981. Formation of N-nitrosodimethylamine During Treatment of Municipal Waste Water by Simulated Land Application. *J. Environ. Qual*., 10(3), 416-421.

Griffin, A.E.; Baker, R.J. (1941). *J. New England Water Works Ass*.55

Griffin, A.E.; Chambelain, N.S. (1956). *Ibid*., No. 3

Hanna, J.V.; Johnson, W. D.; et al. (1991). Characterization of Aqueous Humic Substances before and after Chorination. *Environ. Sci. Technol*., Vol. 25, No. 6, 1991

Hawksworth G.M. and Hill, M.J. (1971). *Brit. J. Cancer*. 25, 520

Hayes, B.T. and Stevens, T.S. (1970). Reduction of nitrosamines to Hydrazines. *J.Chem. Soc*. C1970, 1088-1089

Hayes, M. H. B.; MacCarthy, P.; et al. (1989). Humic Substances II-In Search of Structures. J. Wiley and Sons: New York, 1989

HEEP. 1980. Health and Environmental effects Profile. Nitrosamines, No. 137. Washington D.C.: U.S. Environmental Protection Agency, Office of Solid Waste and Emergency Response.

Hine, J. (1956) Physical Organic Chemistry. McGraw-Hill, New York, N.Y., Toronto, London, 140

Hazardous Substances Data Base (HSDB) (2000). National Library of Medicine. http://toxnet.nlm.nih.gov/cgi-bin/sis/htmlgen?HSDB.

Hughes, E.D.; Ingold, C.K.; Ridd, J.H. (1958a). Nitrosation, Diazotisation, and Deamination. Part I. Principles, Background, and Method for the Kinetic Study of Diazotisation. *J. Chem. Soc.* 58

Hughes, E.D.; Ingold, C.K.; Ridd, J.H. (1958b). Nitrosation, Diazotisation, and Deamination. Part VI. Comparative Discussion of Mechanisms of N- and O-Nitrosation with Special Reference to Diazotisation. *J. Chem. Soc.* 88

International Agency for Research on Cancer (IARC). (1978). Some N-Nitroso Compounds. IARC Monographs on the Evaluation of Carcinogenic Risk of Chemicals to Humans, Vol.17. Lyon, France: International Agency for Reserch on Cancer. 365 pp.

Isaac, R.A. and Morris, J. (1983). Transfer of Active Chlorine from Chloramine to Nitrogenuous Organic Compounds. 1. Kinetics. *Environ. Sci. Technol.* 17, 738-742.

Jafvert, C.T. and Valentine, R.L. (1992). Reaction scheme for the chlorination of ammoniacal water. *Environ. Sci. Technol.* 26(3), 577-86

Jenkins, S.W.D.; Koester, C.J.; Taguchi, V.Y., Wang, D.T.; Palmentier, J.P.F.P., and Hong, K.P. (1995). N- N itrosodimethylamine in drinking water using a rapid, solid-phase extraction method. *Environ. Sci. Pollut. Res*. 2(4), 207-210.

Johnson, J.D.; Inman, G.W. (1977). Annual Report June 1, 1977 to May 31, 1978 prepared for U.S. Nuclear Regulatory Commission under Contract No. NRC-04-77-119.

Keefer, L.K. and Roller P.P. (1973). N-nitrosation by nitrite ion in neutral and basic medium. *Science.* 181, 1245-1247

Kiefer, D.M. (1972). Chem. Eng. News. 50 (51), 9

Kimoto, W.I.; Dooley, C.J.; Carre, J.; and Fiddler, W. (1981). Nitrosamines in tap water after concentration by a carbonaceous adsorbent. *Water Res.* 15, 1099-1106

Kobylinski, E.A.; Peterman, B.W. (1979). Evaluation of Ozone Oxidation and UV Degradation of Dimethylnitrosamine. 7908, 1-16, U.S. Army Medical Research and Development Command: Fort Detrick, Frederick, Maryland.

Kohut, K. D., and Andrews, S. A. (2002). N-nitrosodimethylamine formation in Drinking water due to amine-based polyelectrolytes. *American Water Works Association, Water Quality Technology Conference Proceedings*. 2002, Seattle, WA

Leenheer, J.A. (1981). Comprehensive approach to preparative isolation and fraction of dissolved organic carbon from natural waters and wastewaters. *Environ. Sci. Technol.*, 15, 578-587

Leenheer, J.A. and Noyes, T.I. (1984). A filtration and column adsorbent system for on-site concentration and fractionation of organic substances from large volumes of water. U.S. Geological Survey, Water Supply, Paper no. 2230. Washington DC: U.S. Government Printing Office.

Lijinsky, W. and Epstein, S.S. (1970). Nitrosamines as environmental carcinogens. *Nature (London)* 225, 21-23

Lunn, G. and Sansone, E.B. (1994). Oxidation of 1,1-dimethylhydrazine (UDMH) in aqueous solution with air and hydrogen peroxide. *Chemosphere* 29(7), 1577-1590

Lunn, G.; Sansone, E.B.; and Anderews, A.W. (1991). Aerial oxidation of hydrazines to nitrosamines. *Environ. Mol. Mutagen.* 17, 59-62.

Maeda, K. and K. Tonomura. 1971. Microbial degradation of tetramethylthiuram disulfide (In Janpanese). Kogyo Gijutsuin Hakke Kenkyusho Kenkyu Hokoku. No. 33, 1-8. Chem. Abstr. 74:10620.

Malcolm, R.L. and MacCarthy, P. (1992). Quantitative Evaluation of XAD-8 and XAD-4 Resins Used in Tandem for Removing Organic Solutions from Water. *Environment International.* 18, 597-607

Margerum, D.W.; Schurter, L.M.; Hobson, J.; Moore, E.E. (1994). Water Chlorination Chemistry: Nonmetal Redox Kinetics of Chloramine and Nitrite Ion. Environ. Sci. Technol. 28(2), 331-337

Margerum D.W., Gray, E.T.; and Huffman, R.P. (1978). Chlorination and the formation of N-chloro compounds in water treatment. In Organometals and Organometalloids, Occurrence and Fate in the Environment (Edited by Brinkman F.E. and Bellama J. M.) 278-291

Margerum, D.W.; Gray, E.T., Jr.; Huffman, R.P. (1978). Chlorination and the Formation of N-Chloro Compounds in Water Treatment. In Organometals and Organometalloids: Occurrence and Fate in the Environment; Brinckman, F.E., Bellama, J.M., Eds.; Am. Chem. Soc. Symp. Ser. 82,: Washinton, D.C., 278-291

Merck. (1983). The Merck Index, 10th ed. Rahway, NJ: Merck & Company, Inc.

Mills, J.F. (1979). Bromine Chloride-An Alternative to Chlorine for Treatment of Once Through Cooling Waters. Presented before the Electric Power Research Institute, Condenser Biofouling Control Symposium, Altanta, GA. March 1979

Mirvish, S.S. (1970). Kinetics of dimethylamine nitrosation in relation to nitrosamine carcinogenesis. *J. Nat. Cancer Inst*. 44, 633-639

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

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

Mitch, W.A. and Sedlak, D.L. (2002b). Factors controlling nitrosamine formation during wastewater chlorination. *Water Sci. Technol. Water Supply.* 2(3), 191-198

Mitch, W.A. and Sedlak, D.L. (2002c). Prevention of NDMA formation during chlorination. Presentations at the 4th Symposium in the Series on Groundwater Contaminants: Perchlorate and NDMA in Groundwater: Occurrence, Analysis and Treatment: Groundwater Resources Association of California, April 17, Baldwin Park, CA

Mitch, W.A.; Sharp, J.O.; et al. (2003). N-nitrosodimethylamine (NDMA) as a drinking water contaminant: A review. *Environmental engineering science*. Vol.20, No.5, 2003

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

MOE. (1990). Ontario Ministry of the Environment. Method E3291A. The determination of NDMA in water by GC-HRMS.

MOE. (1998). Ontario Ministry of the Environment. Drinking Water Surveillance Program, 1996-1997 Executive Summary Report, http://www.ene.gov.on.ca/programs/3554e01.pdf (Accessed on August 2005)

MOE. (2003). Ontario Ministry of the Environment. Technical Support Document for Ontario Drinking Water Standards, Objectives and Guidelines. http://www.ene.gov.on.ca/envision/gp/4449e01.pdf (Accessed on August 2005)

Montgomery Watson Harza (MWH, revised by John C. Crittenden et al., 2005). Water Treatment: Principles and Design (2nd Edition). John Wiley & Sons, Inc., Hoboken, New Jersey.

Morris, C. J. (1967). Kinetics of Reactions Between Aqueous Chlorine and Nitrogen Compounds. *Principles and Applications of Water Chemistry. Faust, S.D.; Hunter, J.V.*. Wiley, New York, N.Y., 23

Morris, C. J. and Isaac, R.A. (1981). A critical review of kinetic and thermodynamic constants for the aqueous chlorine-ammonia system. *Water Chlorination: Environ. Impact Health Eff.* (1983), 4(Book 1), 49-62.

Moore, E.W.(1951). Fundamentals of Chlorination of Sewage and Waste. Water & Sewage Works, 98 (3), 130-136

Najm, I. and Ma, J. (2002). Formation of nitrosamines as by-products of chloramination. In *Proceedings of Annual AWWA Conference*. New Orleans.

Najm, I. and Trussell, R.R. (2001). NDMA formation in water and wastewater. *J.AWWA*. 93, 92-99

OEHHA. Office of Environmental Health Hazard Assessment (2006). Draft Public Health Goal for N-Nitrosodimethylamine in drinking Water. http://www.oehha.ca.gov/water/phg/pdf/ndma_draft.pdf

Ohta, T.; Suzuki, J.; Iwano, Y. and Suzuki, S. (1982). Photochemical nitrosation of dimethylamine in aqueous solution containing nitrite. Chemosphere. 11(8), 797-801.

Omietanski, G.M. and Sisler, H.H. (1956). The reaction of chloramine with tertiary amines. 1,1-trisubstituted hydrazinium salts. *J. Am. Chem. Soc.* 78, 1211-1213

Ontario Ministry of Environment and Energy (OMEE) (1994). Removal of N-Nitrosodimethylamine from the Ohsweken (Six Nations) *Water Supply*.

Occupational Safety & Health Administration (OSHA) (2006).
www.osha.gov/pls/oshaweb/owadisp.show_document?p_id=10020&p_table=STANDARDS

Ohshima, H.; and Kawabata, T. (1978). Mechanism of N-nitrosodimethylamine formation from trimethylamine and trimethylaminoxide. In E.A. Walker et al., Eds., *Environmental Aspects of N-Nitroso Compunds: Proceedings of a Working Conference Held at the New England Center for Continuing Education, University of New Hampshire, Durham, New Hampshire, USA, 22-24 August*, International Agency for Research on Cancer Scientific Publication 19; Lyon, France, 143-153

Palin, A. T. (1952). *J. Amer. Water Works Ass*., 44, 48

Plomley, J.B.; Koester, C.J.; March, R.E. (1994). Determination of N-nitrosodimethylamine in Complex Environmental Matrices by Quadrupole Ion Storage Tandem Mass Spectrometry Enhanced by Unidirectional Ion Ejection. *Anal. Chem.*, 66, 4437

Polo, J. and Chow Y.L. (1976). Efficient degradation of nitrosamines by photolysis. *IARC Scientific Publications,* 14, 473-86

Poocharoen, G.; Barbour, J.F.; Libbey, L.M. (1992). Precursors of N-nitrosodimethylamine in Malted Barley. 1. Determination of Hordenine and Gramine. *J. Agric. Food Chem*., 40, 2216

Pressley, T. A.; Bishop, D. F., et al. (1972). Ammonia-Nitrogen Removal by Breakpoint Chlorination. *Environmental Science & Technology*, 6(7), 622-628

Ridd, J.H. (1961). Nitrosation, diazotization, and deamination. *Quart. Rev. Chem. Soc. (London)* 15, 418-441

Rostad, C.E.; Leenheer, J.A.; Katz, B.; Martin, B.S.; and Noyes, T.I. (2000). Characterization and Disinfection By-Product Formation Potential of Natural Organic Matter in Surfaceand Ground Waters from Northern Florida. ACS Symposium Series (2000), 761(Natural Organic Matter and Disinfection By-Products). 154-172.

Rolle, I.; R. Payer; and C. J. Soeder. 1971. Uber die Amine einzelliger Grunalgen. I. Der Spermidingehalt von Scenedesmus acutus (276-3a) und Chlorella fusca (211-8b). *Arch. Mikrobiol.* 77: 185-195

Saiz-Jimenez, C.. Origin and Chemical Nature of Soil Organic Matter. Delft University Press: Delft, The Netherlands, 1988

Sakevich, A. I. 1970. Detection of methyl amines in the culture o fStephanodiscus hantzschii (In Russian). Gidrobiol. Zh. 6: 98-100. Chem. Abstr. 73: 117155(1970)

Sander, J. and Schweinsberg, F. (1972). Wechselbeziehungen zwischen Nitrat, Nitrit und kanzerogenen N-Nitrosoverbindungen. *Zbl. Bakt. Hyg. B* 156, 299-340

Sasajima, M. 1968. Studies on psychrotolerant bacteria in fish and shellfish. III. Reduction and decomposition of trimethylamine oxide by psychrotolerant bacteria (In Japanese). Tokaiku Sursan Kenkyusho Kenkyu Hokoku. 55: 205-214. Chem. Abstr. 73:32608 (1970)

Sax, N.I.; Lewis, R.J.; Sr. Eds. (1987). Hawley's Condensed Chemical Dictionary, 11th ed.; Van Nostrand Reinhold: New York; p 832

Scanlan, R.A.; Lohsen, S.M.; Bills, D.D.; Libbey, L.M. (1974). Formation of dimethylnitosamine from dimethylamine and trimethylamine at elevated temperatures. *J. Agr. Food Chem.* 22, 149-151

Scanlan, R.A.; Barbour, J.F.; Hotchkiss, J.H.; Libbey, L.M. (1980). N-nitrosodimethylamine in beer. *Food Cosmet. Toxicol.* 18(1), 27-9

Sen N.P.; Seman S.; McPherson M. (1980). Further studies on the occurrence of volatile and non-volatile nitrosamines in foods. *IARC Scientific Publications*, 31, 457-65

Shapley, D. (1976). Nitrosamines: Suspects on the trail of prime suspect in urban cancer. *Science.* 191, 268-270

Shukairy, H.M.; Miltner, R.J.; and Summers, R.S. (1995). Bromide's effect on DBP formation, speciation, and control: part 2, biotreatment. J.AWWA. 87(10), 71-82

Siddiqui, Mohamed; and Khalil Z. Atasi (2004). N- nitrosodimethylamine: A disinfectant byproduct and its occurrence in wastewater. Water Environment Research, 76(4), 316-326

Sittig, M. (1985). Handbook of Toxic and Hazardous Chemicals and Carcinogens, 2nd Edition. Park Ridge, NJ: Noyes Publications. 950 pp.

Smith, P.A.S. (1966). *The Chemistry of Open-Chain Organic Nitrogen Compounds*. Vol. 2. Benjamin, New York.

Smith, P.A.S. and Pars, H.G. (1959). Nitrosative cleavage of N',N-dialkylhydrazides and tertiary amines. J. Amer. Chem. Soc. 24, 1325-1332

Smith, T.A. 1971. The occurrence, metabolism and functions of amines in plants. *Biol. Rev.* 46: 201-241

Spincer D.and Westcott, D.T. (1976). Formation of nitrosodimethylamine in smoke from cigarettes manufactured from different tobacco types. *IARC Scientific Publications,* 14, 133-9

Stevens, A.A.; Slocum, C.J.; et al. (1976). Chlorination of organics in drinking water. *J.AWWA*, 1976, 68:615

Stevens, A.A. and Symons, J.M. (1977). Measurement of Trihalomethane and Precursor Concentration Changes. *J.AWWA*, 1977, 546-554

Stojanovia, B.J. and M. Alexander. 1958. Effect of inorganic nitrogen on nitrification. *Soil Sci.* 86, 208-215

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

Tate, R.L.III and Alexander, M., 1975. Stability of Nitrosamines in Samples of Lake Waters, Soil, and Sewage. *Journal of the National Cancer Institute*, 54(2), 327-330.

Taras, M.J.(1953). Effect of Free Residual Chlorination on Nitrogen Compounds in Water. *J. Amer. Water Works Ass*., 45 (1), 47

Thurman, E.M. (1985). *Organic Geochemistry of Natural Waters*, Martinus Nijhoff-Dr. Junk Publishers, Dordrecht

Thurman, E.M. (1986). Dissolved Organic Compounds in Natural Waters. *Organic Carcinogens in Drinking Water: Detection, Treatment, and Risk Assessment.* John Wiley & Sons, New York. 55-92

Thurman, E.M. and Malcolm.R.L. (1981). Preparative Isolation of Auatic Humic Substances. *Environ. Sci. & Tech.,* 15:463-466

Tomkins, B.A. and Wayne H.Griest; Higgins, C.E.. (1995). *Anal. Chem*. 67, 4387-4395

Tomkins, B.A. and Wayne H.Griest. (1996). Determination of at part-per-trillion concentrations in contaminated groundwaters and drinking waters featuring carbon-based membrane extraction disks. *Anal. Chem*. 1996, 68(15), 2533-2540

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

Trofe, T.W.; Inman, G.W.; Johnson, J.D. (1980). Kinetics of monochloramine decomposition in the presence of bromide. *Environ. Sci. Technol*. 14, 544-549.

Turney, T.A. and Wright, G.A. (1959). Nitrous acid and nitrosatioin. *Chem. Rev.* 59, 497-513

U.S. Department of Health and Human Services, Public Health Service, National Toxicology Program. (2005). Report on Carcinogens (ROC), Eleventh Edition. http://ntp.niehs.nih.gov/index.cfm?objectid=32BA9724-F1F6-975E-7FCE50709CB4C932. (Accessed on August 2006)

U.S. EPA. U.S. Environmental Protection Agency (1992). Multi-Media Investigation Manual. http://www.epa.gov/compliance/resources/publications/civil/programs/neic_mmm.pdf (Accessed Sept. 2006)

U.S. EPA. (1996). SW-846: Test Methods for Evaluation Solid Wastes: Physical/Chemical Methods. Publication 955-001-00000-1. Washington, DC: U.S.Government Printing Office, Office of Solid Waste (OSW).

U.S. EPA. (2002). Integrated Risk Information System. Office of Research and Development (ORD), National Center for Environmental Assessment; http://www.epa.gov/ngispgm3/iris/search.htm

U.S. EPA. U.S. Environmental Protection Agency (2005a). http://cfpub.epa.gov/iris/quickview.cfm?substance_nmbr=0045 (accessed Sept. 2005)

U.S. EPA. U.S. Environmental Protection Agency (2005b). http://epa.gov/safewater/mdbp/mdbp.html#st1 (accessed Sept. 2005)

U.S. EPA. U.S. Environmental Protection Agency (2006). http://www.epa.gov/compliance/resources/policies/incentives/auditing/hazardous.pdf (accessed Sept. 2006)

U.S. FDA. U.S. Food and Drug Administration (2006). http://www.cfsan.fda.gov/~lrd/fdaact.html

Valentine, R.L. and Jafvert, C.T. (1988). General Acid Catalysis of Monochloramine Disproportionation. *Enrion. Sci. Technol*., 22, 691-696

Van Rheenen, D.L. 1962. Determination of biogenic amines in faeces of normal dairy cattle. *Nature (London).* 193-170-171

Water Quality Division Disinfection Committee. 1992. Survey of water utility disinfection practices. *Am Water Works J.* 84, 121-128

Weerasooriya, S.V.R. and Dissanayake, C.B. (1989). The enhanced formation of N-nitrosamines in fulvic acid mediated environment. Toxicol. Environ. Chem. 25, 57-62

Wilczek, A.; Assadi-Rad, A.; Wong, C.; Berger, R.;Hunsinger, R.; Smith, J.; Rodigari, F.; Lazzelle, L.; Heaney, C.; Lai, H.; et al. (2002). Screening of treatment process for NDMA control. In *Proceedings of Annual AWWA Conference*. New Orleans.

Wu, W.W.; Chadik, P.A.; and Delfino, J.J. (2003). The relationship between disinfection by-product formation and structural characteristics of humic substances in chloramination. *Environ. Toxicol. Chem.* 22(12), 2845-2852

Yagil, G. and Anbar, M. (1962). The kinetics of hydrazine formation from chloramine and ammonia. *J. Am. Chem. Soc.* 84, 1797-1803

Yoo, J.L.; Fitzsimmons, S.; et al.(2001). Simultaneous Determine of 1.4-Dioxane and N-Nitrosodimethylamine From Drinking Water by GC/MS Using Positive Chemical Ionization. *American Water Works Association, Water Quality Technology Conference Proceedings*. Nashville, TN; 2001, Nov.

Yoo, L.J.; and Fitzsimmons, S.; et al. (2000). Determination of N-nitrosodimethylamine at part-per trillion levels using positive chemical ionization from aqueous samples. *American Water Works Association, Water Quality Technology Conference Proceedings*. Salt Lake City, UT; 2000, Nov.

Yoon, J. and Jensen, J.N. (1993). Distribution of Aqueous Chlorine with Nitrogenous Compounds: Chlorine Transfer from Organic Chloramines to Ammonia. *Environ. Sci. Technol.* 27, 403-409

Yutaka, I. (1967). *Bull. Chem. Soc. Jap.*, 40, 835

VITA

Xianghua Luo was born in Changsha, Hunan, People's Republic of China, the daughter of Xianbao Luo and Lizhen Jiang. She attended No. 1 Middle School Attached to Central China Normal University in Wuhan, Hubei, P.R.China, and graduated in 1991 from the same school. Thereafter, she went to Wuhan Institute of Chemical Technology in Wuhan, Hubei, P.R.China and received the degree of Bachelor of Science in Chemical Engineering in July 1995. During the following years, she was employed as an assistant professor in Chemical Engineering in the same institute. In August 1998, she went to the master program in chemical engineering in Wuhan Institute of Chemical Technology and received the degree of Master of Engineering in July 2001. In August 2001, she entered the Graduate School of the University of Missouri-Columbia and has been studying her doctor of philosophy degree in the area of Environmental Engineering in the Department of Civil & Environmental Engineering.