Evaluating the Need for Regulations Due to the Impact of Nitrosamines in Public Drinking Water Systems

by

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ABSTRACT

The purpose of drinking water regulations is to keep our drinking water safe from contaminants. This research reviewed federal regulation including the Contaminant Candidate List (CCL) regulatory process, the public health effects of six nitrosamines in drinking water, analyzes of occurrence data from Unregulated Contaminant Monitoring Rule (UCMR 2) and suggests how nitrosamines can be regulated. Currently only total trihalomethanes (THM) and haloacetic acids (HA) are regulated at the federal level. However, California has notification action levels and Massachusetts has guidelines of 10 ng/L for nitrosamine concentration.

Nitrosamine data collected under the UCMR 2 were analyzed to assess the occurrence and the effect of disinfectant type and source water type. The data showed that N-nitrosodimethylamine (NDMA) was detected in drinking water at concentrations higher than the minimum reporting level (MRL) of 2 ng/L. Four nitrosamines including N-nitroso-diethylamine (NDEA), N-nitroso-di-n-butylamine (NDBA), N-nitroso-methylethylamine (NMEA) and N-nitroso-pyrrolidine (NPYR) and very low detections. N-nitroso-di-n-propylamine (NDPA) was not detected in the sample analyses. NDMA was primarily detected in public water systems using chloramines other than chlorine.

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DEFINITIONS

Community water system - A public water system which serves at least 15 service connections used by year-round residents or regularly serves at least 25 year-round residents.

Disinfection byproducts - A compound formed by the reaction of a disinfectant such as chlorine with organic material in the water supply; a chemical byproduct of the disinfection process.

Distribution system maximum residence time - An “active” point (currently providing water to customers) in the distribution system where the water has been in the system the longest.

Entry point to the distribution system - The point at which water is discharged into the distribution system from a well, storage tank, pressure tank, or water treatment plant.

Health Reference Level - Exposure levels that will not cause significant risks of non-cancer health effects. These levels are generally developed from exposure levels that do not produce ill effects in experimental animals.

Maximum contaminant level - The highest level of a contaminant that is allowed in drinking water.

Maximum contaminant level goal - The level of a contaminant in drinking water below which there is no known or expected risk to health.

Maximum residual disinfectant level - The highest level of a disinfectant allowed in drinking water.

National Primary Drinking Water Regulation - Legally enforceable standards that apply to public water systems.

Non-community water system - A public water system that is not a community water system; e.g. the water supply at a camp site or national park. There are two types of NCWSs: transient and non-transient.

Non-transient non-community water systems - A public water system which supplies water to 25 or more of the same people at least six months per year in places other than their residences. Some examples are schools, factories, office buildings, and hospitals which have their own water systems.

Safe Drinking Water Act – A legislative Act passed by Congress in 1974 intended to protect public health by regulating public drinking water supply in the United

States. The law was amended in 1986 and 1996 and requires many actions to protect drinking water and its sources: rivers, lakes, reservoirs, springs, and ground water wells.

Transient non-community water systems - A public water system which provides water in a place such as a gas station or campground where people do not remain for long periods of time.

Unregulated Contaminated Monitoring Program - to collect data for contaminants suspected to be present in drinking water, but that do not have health-based standards set under the Safe Drinking Water Act (SDWA).

Unregulated Contaminant Monitoring Regulation – Requires public water systems to monitor the targeted contaminants on the CCL.

Unregulated Contaminant Monitoring Rule - Requires the EPA to establish a list of up to 30 unregulated contaminants every five years, to be screened for in a representative sampling program.

ACRONYMS

CWS - Community water system

CCL - Contaminant Candidate List

DBPs - Disinfection byproducts

DSMRT - Distribution system maximum residence time

EPTDS - Entry point to the distribution system

GC - Gas chromatography

HAA - Haloacetic acids

HSDB - Hazardous Substances Data Bank

HRL - Health Reference Level

IARC - Integrated Risk Information System

IRIS - Integrated Risk Information System

IESWTR - Interim Enhanced Surface Water Treatment Rule

MCL - Maximum contaminant level

MCLG - Maximum contaminant level goal

MRDL - Maximum residual disinfectant level

NPDWR - National Primary Drinking Water Regulation

NOM - Natural organic matter

NDEA - N-nitroso-diethylamine

NDMA - N-nitroso-dimethylamine

NDBA - N-nitroso-di-n-butylamine

NDPA - N-nitroso-di-n-propylamine

NMEA - N-nitroso-methylethylamine

NPYR - N-nitroso-pyrrolidine

NTNCWS - Non-transient non-community water systems

SDWA - Safe Drinking Water Act

SPE - Solid phase extraction

Stage 1 DBPR - Stage 1 Disinfectants and Disinfection Byproducts Rule

Stage 2 DBPR - Stage 2 Disinfectants and Disinfection Byproducts Rule

SWTR - Surface Water Treatment Rule (SWTR)

TRI - Toxics Release Inventory (TRI)

TNCWS - Transient non-community water systems (TNCWS)

THM - Trihalomethane

USEPA - U.S. Environmental Protection Agency

UCM - Unregulated Contaminant Monitoring

UCMR – Unregulated Contaminant Monitoring Regulation

UCMR - Unregulated Contaminant Monitoring Rule

Chapter 1

INTRODUCTION

Overview

The U.S. Environmental Protection Agency (USEPA) is required by the 1996 Safe Drinking Water Act (SDWA) Amendments (section 1412(b)(1)) to publish a list of currently unregulated contaminants that may pose risks for drinking water and to make determinations on whether to regulate at least five contaminants from the list with a national primary drinking water regulation (NPDWR) (Safe Drinking Water Act, 1996). The list is known as the Contaminant Candidate List (CCL), which is the primary source of contaminants for which USEPA conducts research to make decisions about whether regulations are needed (Announcement of the Drinking Water Contaminant Candidate List, 1998). The regulatory process (See Figures 1-3) for the CCL 3 included evaluating approximately 7,500 potential chemical and microbial contaminants, however 600 contaminants were looked at based on risk and likelihood of occurrence in drinking water, and based on that process, a preliminary candidate list for further consideration was created (Drinking Water Contaminant Candidate List 3, 2008).

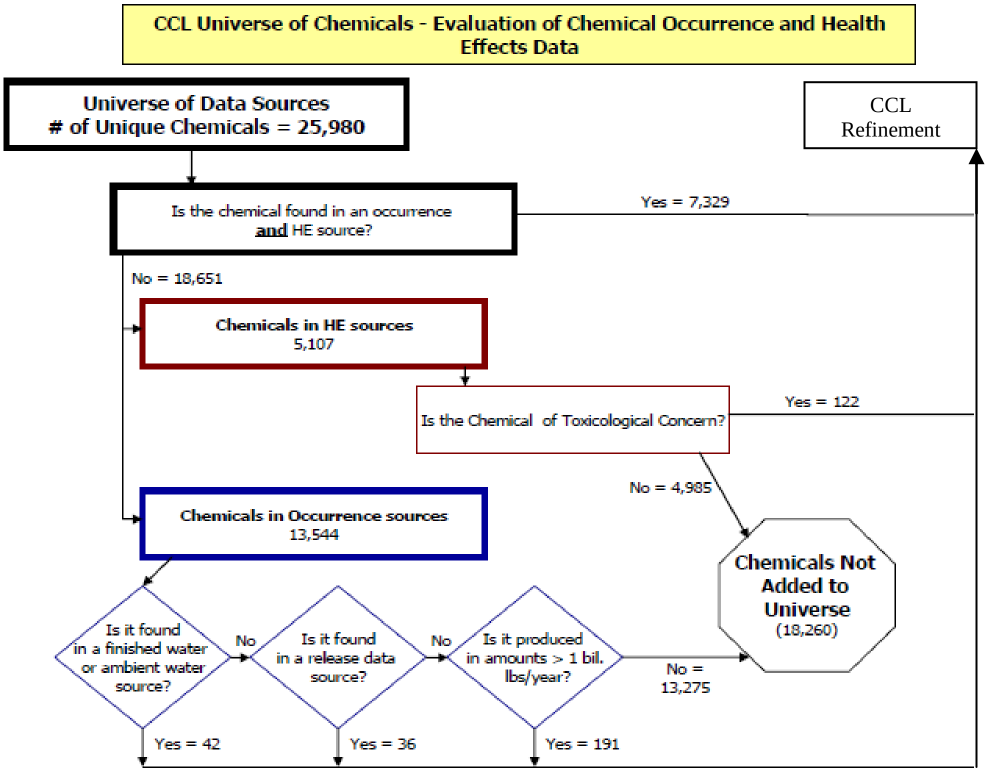

Figure 1: CCL Universe Selection Process (USEPA 2009b)

USEPA then assesses all of these contaminants in more detail to evaluate the likelihood that specific contaminants could occur in drinking water at levels and at frequencies that pose a public health risk (US Environmental Protection Agency [USEPA], 2009b). The end result is a list of contaminants that goes into a draft CCL (Drinking Water Contaminant Candidate List 3-Draft, 2008). The contaminants on the list are known or expected to occur in public water systems. The current list, which has been finalized, is referred to as CCL 3. The list includes 104 chemicals and 12 microbiological contaminants, including chemicals used in commerce, pesticides, biological toxins, disinfection byproducts, and waterborne pathogens (Drinking Water Contaminant Candidate List 3-Final, 2009).

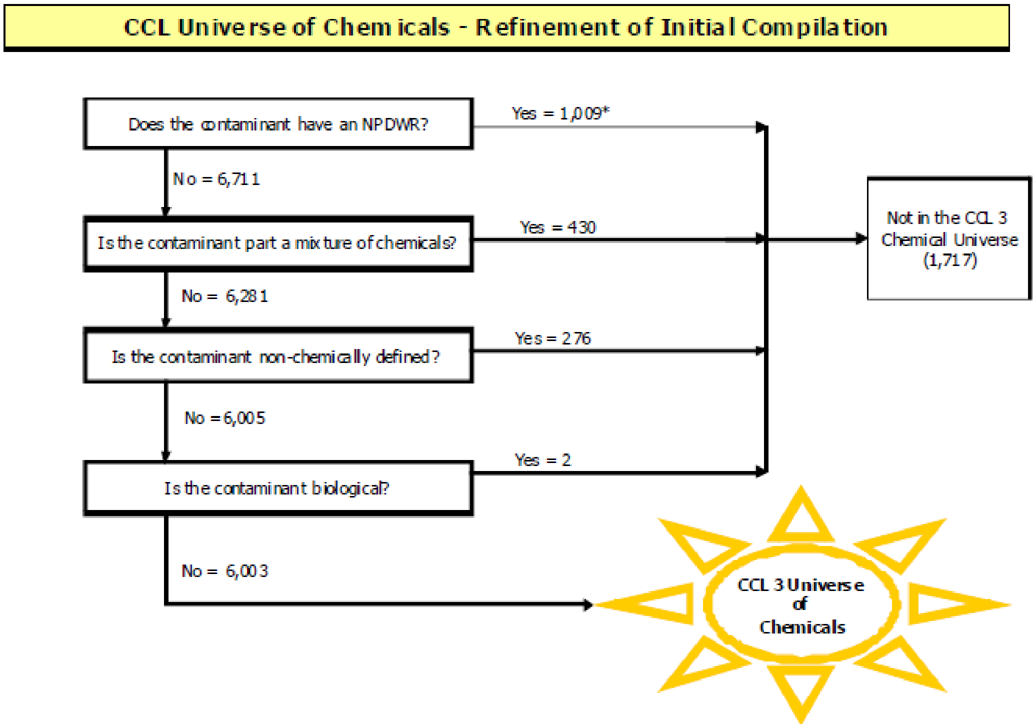

Figure 2: CCL Universe Selection Process: Chemical Refinement (USEPA 2009b)

The CCL 3 contaminants need to be evaluated in more detail to determine if a contaminant has a sufficient amount of data to meet the regulatory determination criteria in the Federal regulation. The characterization of each contaminant included on the CCL requires data in three categories: health effects (HE), occurrence, and analytical methods. Once the list is finalized, it is determined which contaminants need to be monitored. The Unregulated Contaminant Monitoring (UCM) list is developed by using the CCL 3 contaminants. The Unregulated Contaminant Monitoring Regulations (UCMR) requires public drinking systems to monitor for selected contaminants (Unregulated Contaminant Monitoring Regulation (UCMR) for Public Water

Systems Revisions, 2007). In addition, contaminants on the CCL can be eliminated and contaminants can be added to UCMR list of contaminants.

USEPA uses the UCM program to collect data for contaminants that may be present in drinking water, but do not have standards in place under the Safe Drinking Water Act (SDWA). Monitoring is required for no more than 30 contaminants per 5-year cycle. Monitoring is required for only a representative sample of public water systems serving less than 10,000 people. Analytical results from UCMR monitoring are stored in a National Contaminant Occurrence Database (NCOD) (USEPA, 2011).

Research is needed to determine whether sufficient information and/or data are available to identify the potential health effects and the known occurrence in and exposure from water. Health assessments are reviewed to identify potential adverse health effects. USEPA developed the Integrated Risk Information System (IRIS) to evaluate scientific studies and data on human health effects that may result from exposure to contaminants from releases to air, water, and land. Water data is reviewed to determine if the contaminant is likely to occur in drinking water. Figure 3 shows the regulatory process for determining drinking water regulations. Once USEPA review the data from the UCMR, they determine if regulations are needed. If regulations are needed, regulations are developed.

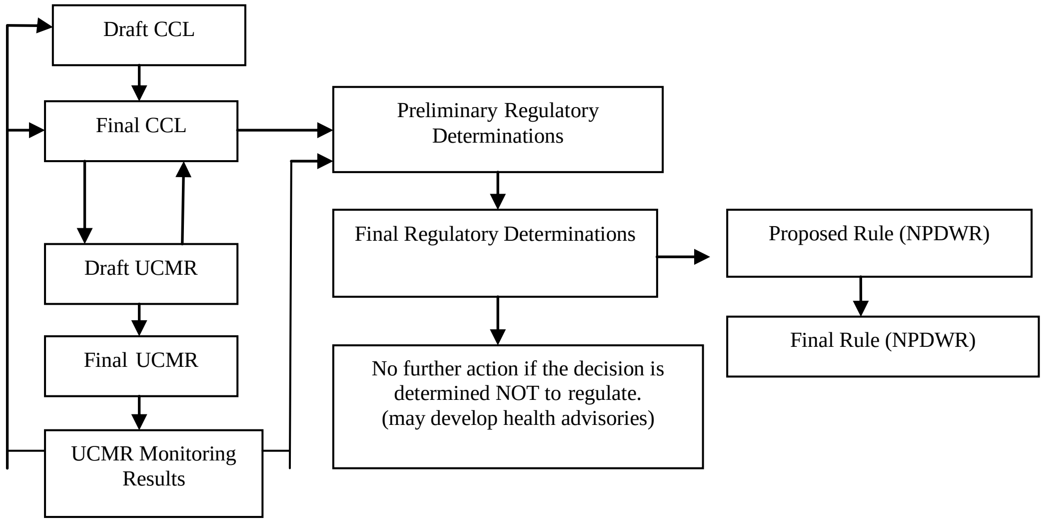

Figure 3: USEPA Regulatory Process

Nitrosamines

According to National Cancer Institute, “a carcinogen is any substance that causes cancer.” However, cancer does not always develop. Animal studies are used to document environmental causes of cancer (American Cancer Society, 2012).

Nitrosamines are known to be probable carcinogenic chemical compounds formed from nitrites and amines (National Toxicology Program [NTP], 2011). Nitrosamines are increasingly becoming known as a health risk and, as a result, regulations on these compounds are expected to increase quickly in the next few years. Laboratory studies have indicated nitrosamines caused various health risks in laboratory animals, including liver, kidney, lung; and stomach cancer (International Agency for Research on Cancer [IARC], 1978). Nitrosamines have the general formula RR′NNO, where R and R′ are side groups with a variety of possible structures. An example of a nitrosamine is dimethylnitrosamine, which has two methyl side groups (CH_3–) (Encyclopedia, 2011).

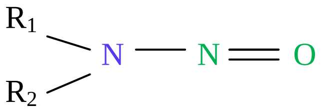

Figure 4: Nitrosamine general structure

Formation of Nitrosamines

Nitrosamines are polar compounds and are usually soluble in water. Their partition coefficients in octanol/water are low and therefore the compounds are difficult to extract with organic solvents. The compounds also are not adsorbed on nonpolar surfaces to any significant extent. The Henry's Law constants are small, which means that nitrosamines cannot be removed from water by aeration. These characteristics of nitrosamines contribute to a large risk of ground water contamination because nitrosamines can penetrate soil. This can cause contamination of the drinking wells. Concentrations in surface waters are relatively low, possibly due to dilution and degradation.

The nitrosation of secondary amines is a well known reaction. Nitrosating compounds can be formed from nitrites, nitrates and nitro compounds. The reaction requires an acidic pH, which yields decreased nitrosation as the pH increases. However, there are several studies that identified additional catalytic mechanisms, such as photochemical reactions, formaldehyde (Keefer & Roller, 1973) or fulvic acid (Weerasooriya & Dissanayake, 1989) may react at neutral or even basic pH (Ayanaba & Alexander, 1976; Leach et al. 1987).

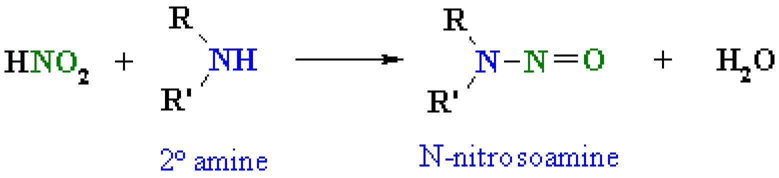

Figure 5: Formation of Nitrosamines

There has been several research studies completed showing how nitrosamines are formed. These include oxidation of dimethylamine (DMA), raw water oxidation with chlorine dioxide or ozone, and lime softening addition. In addition, increased temperature and bromides may form nitrosamines. Also, adding chlorine to water results in some of the organic matter in the water reacting to produce probable carcinogenic byproducts. Additionally, a large source of nitrosamines in the groundwater results from rocket fuel discharge from the aerospace industry. However, the most serious threat for consumers results from the generation of nitrosamines such as N-nitroso-dimethylamine (NDMA) during final disinfection of drinking water with chloramines. The concentration of NDMA increases with distance from the water treatment facility (Barrett et al. 2003; Charrois et al. 2007; Wilczak et. al 2003).

Chloramines have been linked with the formation of nitrosamine (Najm & Trussel, 2001), which reacts with dimethylamine forming unsymmetrical dimethylhydrazine (UDMH) (see Figure 6). UDMH can easily oxidize to various compounds, such as NDMA (Mitch & Sedlak, 2002).

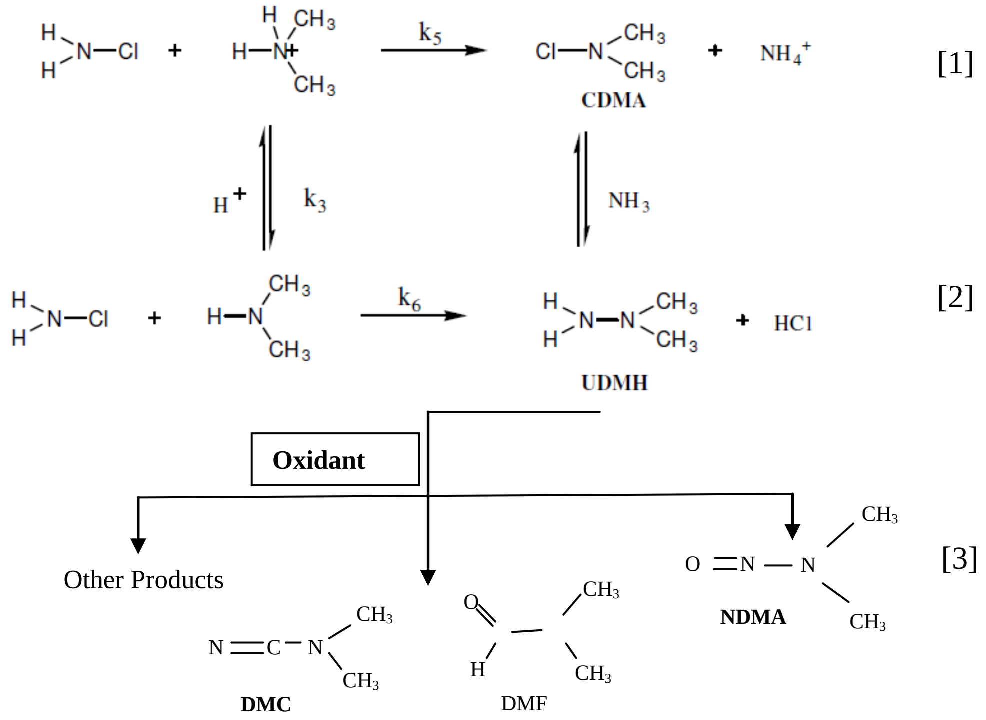

Figure 6: NDMA formation via the UDMH pathway as proposed by Mitch & Sedlak (2002)

Chlorination with nitrite can form nitrosamines (Choi & Valentine, 2003; Schreiber & Mitch, 2007) (see Figure 7). Schreiber and Mitch's (2007) research modified this formation pathway by showing that dichloramine ($NHCl_2$) was the source instead of monochloramine (NH_2Cl) (see Figure 8).

$$HOCl + NO_2 \rightleftarrows NO_2Cl + OH \qquad [1]$$

$$NO_2Cl + NO_2 \rightleftarrows N_2O_4 + Cl \qquad [2]$$

$$NO_2Cl + OH \rightleftarrows NO_3 + H + Cl \qquad [3]$$

$$H + NH_2Cl + NO_2 \rightleftarrows NO_2Cl + NH_3 \qquad [4]$$

$$(CH_3)_2NH + N_2O_4 \rightleftarrows (CH_3)_2\text{-}N\text{-}NO \qquad [5]$$

Figure 7: Nitrosation pathway as proposed by Choi and Valentine (2003)

$$(CH_3)_2NH + HNCl_2 \rightleftarrows (CH_3)_2\text{-}N\text{-}NHCl \qquad [1]$$

$$(CH_3)_2NH\text{-}HNCl + O_2 \rightleftarrows (CH_3)_2\text{-}N\text{-}N{=}O + HOCl \qquad [2]$$

Figure 8: NDMA formation modified by Schreiber and Mitch (2007)

Yang et al proposed that NDMA formation is based on the generation of hydroxylamine as a by-product of DMA oxidation (see Figure 9). The formation of nitrosamines proceeds through UDMH formation and then oxidation of the hydrazine (Yang et al. 2009).

$$\underset{\text{DMA}}{(CH_3)_2NH_2} \overset{H^+}{\longleftrightarrow} \underset{\text{DMA}}{(CH_3)_2NH} \xrightarrow[\text{OH, } O_2, O_3]{\boxed{\text{radicals}}} (CH_3)_2NOH \xrightarrow[\text{OH, } O_2, O_3]{\boxed{\text{radicals}}} NH_2OH \qquad [1]$$

$$(CH_3)_2NH_2 + NH_2OH \longrightarrow \overset{O_3}{(CH_3)_2NNH_2} \longrightarrow (CH_3)_2N_2O \qquad [2]$$

Figure 9: Ozonation pathway as proposed by Yang et al (2009)

There are no Federal regulations in the United States for nitrosamines in drinking water. Due to the high carcinogenic activity of nitrosamines, states have generally set maximum allowable concentration levels at a low ng/L level (for a risk of 10^{-5}) (USEPA, 1980). Most states have primacy over their drinking water regulations and therefore can have more stringent regulations than Federal regulations. This enables the States to ensure even a higher standard for the public health concerns. The lack of firm directives for the maximum allowable amounts of NDMA and other nitrosamines has led to rather arbitrary levels being set, and even more arbitrary enforcement of these regulations.

Several detections in California were found which led the state to develop standards (CPH, 2006). After the discovery of NDMA in California well water, the State of California issued an action level of 2 ng/L for NDMA. However, this action level was increased to 10 ng/L, due to the difficulty in the sampling and analysis technique. The State of Massachusetts has guidelines for 0.00001 ug/L (10 ng/L) based on the findings in California.

In March 2010, Canada proposed a maximum acceptable concentration in drinking water of 0.00004 ug/L (40 ng/L). Ontario has issued an interim maximum acceptable concentration of 9 ng/L for NDMA. The Drinking Water Inspectorate of England and Wales requires monitoring of NDMA at 1 ng/L, while in Germany the permissible health-based values for NDMA and N-Nitrosomorpholine (NMOR) are equal to 10 ng/L.

Thesis Statement

Current disinfectant byproduct regulations only regulate total trihalomethanes (THM) and haloacetic acids (five) (sum of monochloroacetic acid, dichloroacetic acid, trichloroacetic acid, monobromoacetic acid, and dibromoacetic acid) (HAA5) at the federal level. However nitrosamines' occurrence is increasing and they may have a greater health impact on the public.

USEPA has already made the decision that there is potential health risk. This determination provided enough information for nitrosamines to be on the CCL 3. The purpose of this research is to review and analyze the water data for the occurrence of the six disinfection by-products known as N-nitroso-diethylamine (NDEA), N-nitroso-dimethylamine (NDMA), N-nitroso-di-n-butylamine (NDBA), N-nitroso-di-n-propylamine (NDPA), N-nitroso-methylethylamine (NMEA), and N-nitroso-pyrrolidine (NPYR) that was added to the CCL 3 and collected during the UCMR 2.

Scope of Work

The research will focus on nitrosamines on the CCL 3 that are known to be disinfection by-products. The purpose of researching nitrosamines in drinking water is to protect populations from exposure to nitrosamines in drinking water to reduce potential health risks associated with nitrosamines. I will be reviewing water data to see how extensive the problem is.

Objectives

1. Review the literature on adverse health effects from the target contaminants;
2. Analyze the extent of occurrence of the target contaminants in drinking water
3. Analyze the extent of occurrence based on disinfectants used for treatment and water sources
4. Make recommendations

Limitations

This document is intended to provide supporting documentation for technical background information. This can be used to supplement the regulatory determinations being made on the drinking water Contaminant Candidate List (CCL 3). This research does not discuss treatment cost, wastewater treatment impacts, or if laboratories are approved for analytical methods.

The drinking water facilities sampling was conducted throughout the United States. Results may vary for different locations and periods of the year.

Assumptions

1. All sample data gathered for this study comes from the public water systems that were submitted to USEPA for collection and are therefore presumed valid.
2. Nitrosamines samples are required to be analyzed using Method 521.
3. This dataset is complete. UCMR 2 monitoring occurs through December 2010, and data was expected to be reported to USEPA through the summer of 2011.
4. Nitrosamines samples are collected at the maximum residence (MR) time in the distribution system (DS)

Chapter 2

LITERATURE REVIEW

This chapter reviews literature pertinent to the objectives of this thesis. Specifically, it focuses on four main topics:

- Safe Drinking Water Regulation
- Disinfection-By Products
- Selected Nitrosamines and Water
    - Properties
    - Environmental Fate and Behavior
    - Health Effects
- Previous Occurrences
- Sampling and Analytical Techniques

Safe Drinking Water Regulation

A study in 1972 found that 36 chemicals were detected in treated water sampled from water treatment plants that received water from the Mississippi River in Louisiana (USEPA, 1972). New legislative proposals for a federal safe drinking water law were introduced in Congress, due to this study and other similar studies. These studies increased awareness and ultimately led to several federal environmental and health laws dealing with polluted water, hazardous waste, pesticides, etc. One of these laws was the Safe Drinking Water Act (SDWA) of 1974. The purpose of the SDWA is to ensure that public water supplies meet national standards that protect consumers from harmful and dangerous contaminants in drinking water. EPA regulations under the SDWA apply to public water systems. Public water systems can be publicly or privately owned but provide drinking water to a minimum of 25 people or 15 service connections for at least 60 days per year. Consumers who are not served by a public water system use private wells, which are not federally regulated.

SDWA requires USEPA to regulate contaminants that present health risks and are known or most likely, to occur in public drinking water supplies. USEPA sets a non-enforceable health goal, or maximum contaminant level goal (MCLG) for each contaminant requiring federal regulation (Safe Drinking Water Act [SDWA], 1976). An MCLG is the level of a contaminant in drinking water below which there is no known or expected risk to health.   USEPA is then required to establish an enforceable limit, or maximum contaminant level (MCL), which is as close to the MCLG as possible (SDWA, 1976). An MCL may be established, if treatment technology is available, taking cost into consideration. Where analytical methods are not adequately developed to measure the concentrations of certain contaminants in drinking water, EPA specifies a treatment technique, instead of an MCL, to protect against these contaminants (SDWA, 1996).

The 1974 SDWA required EPA to regulate drinking water in two steps. The first step involved developing national interim primary drinking water regulations based, for the most part, on the Public Health Service standards (Safe Drinking Water Act, 1974). These included MCLs, but also established requirements for monitoring and analyzing regulated contaminants in drinking water, reporting analytical results, record keeping, and notifying the public when a water system fails to meet federal standards for any of the contaminants (Safe

Drinking Water Act, 1974). These interim MCLs or standards were developed to be enforceable until revised. The second step involved the revision of these standards, as necessary (USEPA, 1976).

To maintain the public's health, the 1986 Amendments required EPA to set MCLGs and MCLs for 83 named contaminants (this list included the interim standards, except for TTHMs) (Safe Drinking Water Act, 1986). SDWA was amended in 1996, emphasizing comprehensive public health protection through risk-based standard setting, increased funding, confidence in best available science, prevention tools and programs, strengthened enforcement authority for EPA, and public participation in drinking water issues (Safe Drinking Water Act, 1996).

The amendments to the SDWA in 1996 required EPA to give emphasis to comprehensive public health by developing rules to balance the risks between microbial pathogens and disinfection byproducts (DBPs)(Safe Drinking Water Act, 1996). The concern was that the treatment to destroy microbial pathogens was creating DBPs. The Stage 1 Disinfectants and Disinfection Byproducts Rule (Stage 1 DBPR) and Interim Enhanced Surface Water Treatment Rule (IESWTR), promulgated in December 1998, were the first part of the requirement (Stage 1 Disinfectants and Disinfection Byproducts Rule, 1998). The Stage 2 Disinfectants and Disinfection Byproducts Rule (Stage 2 DBPR) adds another layer to the Stage 1 DBPR to handle higher risk public water systems for protection measures beyond those required for existing regulations (Stage 2 Disinfectants and Disinfection Byproducts Rule, 2006). The Stage 2 DBPR and the Long Term 2 Enhanced

Surface Water Treatment Rule (LT2) are the second part of rules required by Congress. These rules strengthen protection against microbial contaminants, particularly *Cryptosporidium*, and at the same time, reduce possible health risks of DBPs (Stage 2 Disinfectants and Disinfection Byproducts Rule [Stage 2 DBP], 2006).

Disinfection-By Products

The purpose of water disinfection is the inactivation of microbes (viruses, bacteria, protozoan etc). Disinfectants are a vital and necessary element of drinking water treatment because of the layer of protection they provide against waterborne microorganisms that cause various diseases (USEPA, 2000). Disinfection byproducts (DBPs) normally form when disinfectants used to treat drinking water react with naturally occurring materials in the water. The use of chlorine is the most popular and cost effective form of disinfection for drinking water. Free chlorine is used as the primary disinfectant and may be used with a secondary disinfectant, such as chloramines, ozone, chloride dioxide, or ultra-violet radiation (LeChevallier & Au, 2004).

Although disinfection of water inactivates microbes that can transmit disease, it has the disadvantage of producing hundreds of DBPs, some of which are considered to be harmful to humans (Carlson & Hardy, 1998; Chen & Weisel, 1998). All surface water systems and groundwater under the direct influence of surface water are required to disinfect under the Surface Water Treatment Rule (SWTR). Community water systems (CWS) and non-transient non-community water systems (NTNCWS) disinfect their water supplies, as well as transient non-community water systems (TNCWS) that use chlorine dioxide, as regulated under the Stage 2 DBPR (Stage 2 DBP, 2006).

Major factors affecting the type and amount of DBPs formed include:

- Disinfectant used, dose, and residual concentration of disinfectant.
- Contact time and mixing conditions between disinfectant (oxidant) and precursors.
- Concentration and characteristics of precursors.
- Water temperature.
- Water chemistry.

Disinfectant used, dose, and residual concentration of disinfectant. Disinfectants include chlorine, chlorine dioxide, chlorite, and ozone. Most water systems that disinfect use either liquid (NaOCl) or gaseous chlorine (Cl_2), as their disinfectant. As the concentration of disinfectants such as chlorine or chloramines increases, the production of DBPs increases. Formation reactions continue as long as precursors and disinfectant are present (Krasner, 1999).

Chlorine reacts with natural organic matter (NOM) to form halogenated byproducts. In addition, brominated byproducts are formed when source water containing bromide is chlorinated (Rook, 1974). Chlorine reacts with NOM in the water to form THMs, HAAs and other disinfection byproducts (Richardson, 2002)

Chlorine dioxide can also oxidize bromide ions to bromine. The bromine can then react with organic matter to form brominated DBPs (Pourmoghaddas & Stevens, 1995; Cowman & Singer, 1996). Chlorite can react with excess chlorine to reform chlorine dioxide. Some systems may opt to boost with chlorine to maintain a residual in the distribution system. If doses are high enough, systems could exceed either the chlorine dioxide maximum residual disinfectant level (MRDL) or the chlorite MCL (USEPA, 2012). The MRDL is defined as a level of a disinfectant added for water treatment that may not be exceeded at the consumer's tap (USEPA, 2006). The increased chlorine dioxide can also volatilize at consumer's faucets and react with volatile organics to cause odor problems (USEPA, 2006).

Ozone does not directly produce chlorinated DBPs (Cho et al., 2003). However, a mixture of bromo-chloro DBPs as well as chlorinated DBPs can form, if chlorine is added before or after ozonation (USEPA, 2006). Ozone can modify the characteristics of precursors and change the concentration and speciation of halogenated DBPs (THMs and HAAs) when chlorine is added downstream (Cho et al., 2003).

Contact time. When the reaction time is shorter, increased concentrations of trihalomethanes (THM) and halogenic acetic acids (HAA) may be formed. When the reaction time is longer, some temporary forms of disinfection byproducts may become disinfection byproducts, such as tribromine acetic acid or bromoform. Whereas, temporary forms of disinfection byproducts could decompose if the contact time decreased.

Precursors. Organic DBPs (and oxidation byproducts) are formed by the reaction between organic substances and oxidizing agents that are added to water during treatment. In most water sources, NOM is the major component of organic substances and DBP precursors. Organic substances and DBP precursors in water also come from a variety of other sources, including storm water and wastewater. Rain events wash organic matter into surface water and ground water that has NOM is an indication that the water is under direct influence of surface water.

Water temperature. When temperatures increases, reactions take place faster, causing a higher chlorine concentration to be required for a proper disinfection (USEPA, 2006). This causes more halogenic disinfection byproducts to form. An increase in temperatures also enhances the decomposition of tribromine acetic acids, HAN and HK.

Water chemistry. When pH values are high, more hypochlorite ions are formed, causing chlorine disinfection to decrease (USEPA, 2006). At higher pH values, more THM is formed; whereas more HAA is formed when pH values are lower (Stevens et al., 1989). At high pH values, HAN and HK are decomposed by hydrolysis, because of an increase in hydrolysis reactions at higher pH values.

There are up to 600 DBPs that have been identified but only a fraction of them — including bromate, total trihalomethanes (chloroform, bromodichloromethane, dibromochloromethane and bromoform) and haloacetic acids (dichloroacetic acid, trichloroacetic acid, monochloroacetic acid, monobromoacetic acid and dibromoacetic acid) — are monitored by the USEPA (Richardson et al., 2008).

Increased interest in nitrosamines is due to population growth, which has forced utilities to consider other sources for drinking waters due to impaired source water with significant concentration of wastewater effluents or algal blooms (Shad et al., 2012). In addition, to reduce the formation of THMs and

HAAs, utilities are experimenting with alternatives to chlorine disinfection. However, some of these emerging disinfectant combinations reduce THMs and HAAs while forming nitrosamines.

Nitrosamines and Water

The SDWA requires USEPA to periodically publish a CCL. The first published lists were CCL 1 with 60 contaminants in March 1998 and the CCL 2 with 51 contaminants in February 2005 (USEPA, 1998; USEPA, 2005a). USEPA published the third CCL (CCL 3) on February 21, 2008 (USEPA, 2008). The final list was published on October 8, 2009 in the Federal Register (FR) (USEPA, 2009). Once the CCL is published, USEPA conducts research, makes regulations determinations, and moves forward to develop regulations as needed.

The nitrosamine NDMA has become of increasing concern because it is formed during the process of treating water before delivery and is a potent carcinogen, with a theoretical 10^{-6} lifetime cancer risk level at exposures of 0.7 ng/L. Due to public health concerns for the impact of nitrosamines in drinking water, USEPA added this contaminant to the CCL 3 list. The following nitrosamines are the contaminants of concern: N-nitroso-diethylamine (NDEA), N-nitroso-dimethylamine (NDMA), N-nitroso-di-n-butylamine (NDBA), N-nitroso-di-n-propylamine (NDPA), N-nitroso-methylethylamine (NMEA), and N-nitroso-pyrrolidine (NPYR) that was collected during the UCMR.

N-nitroso-diethylamine

Properties and Sources. N-nitroso-diethylamine (NDEA) is a volatile, slightly yellow liquid with no characteristic odor that is soluble in water, alcohol, ether, other organic solvents, and lipids. The vapor pressure is 0.86 mm Hg at 20 °C and the estimated adsorption coefficient (Koc) is 43 (log Kow of 0.48). The estimated Henry's Law constant is 1.1X10^{-8} atm-cu m/mol. (ChemIDPlus, 2004a) NDEA is sensitive to light, particularly ultraviolet light, and undergoes partial photolytic degradation. When heated to decomposition, NDEA emits toxic fumes of nitrogen oxides (Integrated Risk Information System [IARC], 1993a). NDEA is used primarily as a research chemical. In addition, it is used as an additive to gasoline and lubricants, antioxidant and stabilizer in plastics (Hazardous Substances Data Bank [HSDB], 2003a).

Environmental fate and behavior. According to the Hazardous Substance Data Base (HSDB), NDEA has been released into the environment from industrial sources, such as the rubber, dye and metal industries, as well as from cigarette smoke. Environmental releases of NDEA included 11,795 lb of waste containing NDEA released by three facilities in 1999, 99.6% of which was released to land. In 2007, a facility released 500 lb of NDEA to a hazardous-waste landfill. From 2008 to 2010, a facility released 2, 237 lbs of NDEA to a hazardous-waste landfill (Toxics Release Inventory [TRI], 2012a).

Air -- Vapor pressure measurement estimate NDEA will exist as a vapor in ambient atmosphere. The half-life was calculated to be about 1-2 hours in a Teflon outdoor smog chamber irradiated with sunlight. (HSDB, 2003a) The estimated atmospheric residence time is <0.3 days with the decomposition induced by light or other radiant energy.

Water -- NDEA is expected to stay in solution and not partition onto organic matter due to its estimated Koc value. The Henry's Law constant indicates volatilization from water will probably be small. In one study, it was shown that photolysis may be the most significant removal process because 89% of the degradation occurs in 7 hours with sunlight (HSDB, 2003a).

Soil -- The estimated Koc value also indicates that NDEA is moderately to highly mobile in soil. Volatilization will probably be rapid from soil surfaces; however volatilization of NDEA mixed into the soil will not be as rapid but may be considerable. One study found that NDEA at a concentration of 18.0 ppm nitroso-N slowly disappeared in soil after several weeks. (HSDB, 2003a) The half-life seemed to be about 3 weeks in the Matapeake loam at 30 °C. The primary removal mechanisms were volatilization (significant during the first few days) and biodegradation (HSDB, 2003a).

Health Effects. NDEA has been found to be carcinogenic in several animals that developed benign and malignant tumors after being exposed by NDEA via various routes including ingestion, injection, and inhalation (IARC, 1993). No epidemiological studies are known that evaluate the relationship between exposure to NDEA and human cancer (National Toxicology Program [NTP], 2011).

N-nitroso-dimethylamine

Properties and Sources. N-nitroso-dimethylamine (NDMA) is a volatile, yellow oily liquid with a faint characteristic odor that is soluble in water, alcohol, ether, other organic solvents, and lipids. The vapor pressure is 2.7 mm Hg at

20 °C. The estimated adsorption coefficient (Koc) is 12 (log Kow of -0.57). The estimated Henry's Law constant is 1.82X10^{-6} atm-cu m/mol (ChemIDPlus, 2004b). NDMA is sensitive to light, particularly ultraviolet light, and undergoes rapid photolytic degradation (IARC 1978, HSDB 2003b). NDMA can be produced and released from industrial sources through chemical reactions, such as those that involve alkylamines with nitrogen oxides, nitrous acid, or nitrite salts. Industrial sources include byproducts from tanneries, pesticide and rocket fuel manufacturing plants, rubber and tire manufacturers, fish processing facilities, foundries, and dye manufacturers (ATSDR, 1989b). NDMA is used mainly as a research chemical. In addition, it has been used as an additive for lubricants, an antioxidant, and a softener of copolymers (ATSDR, 1989b; HSDB, 2008b).

Environmental fate and behavior. NDMA contamination may be found in air, soil, and water (ATSDR, 1989b). Environmental releases of NDMA have been to landfills, since 1998. In 2006, two facilities released 799 lbs of NDMA to an off-site hazardous-waste landfill (TRI, 2012b).

Air -- When released to the air, NDMA is broken down quickly by sunlight (ATSDR, 1989b). The vapor pressure measurement estimates NDMA will exist as a vapor in ambient atmosphere. The half-lives were calculated to be about 5 minutes, approximately 30 minutes, and less than or equal to 0.3 days (7.2 hours) (HSDB, 2003b). The estimated atmospheric residence time is 6.3 days with the decomposition induced by light or other radiant energy.

Water -- NDMA is completely miscible and does not gather onto solid particles or sediment based on its Koc (HSDB, 2003b). This compound's measured Henry's Law constant indicates that volatilization from water surfaces is expected to occur. Estimated volatilization half-lives from models of a river and lake are 17 and 130 days, respectively. A photodegradation half-life of 79 hours was measured in distilled water exposed to fluorescent light through a pyrex filter (Polo & Chow, 1976). No biodegradation of NDMA was observed in lake water samples during an observation period of 3.5 months (HSDB, 2003b).

Soil -- NDMA can be highly mobile and has the potential to leach into ground water (ATSDR, 1999; HSDB, 2008b). Volatilization from wet soil surfaces may occur based upon a measured Henry's Law constant. NDMA may volatilize from dry soil surfaces based upon its measured vapor pressure. A half-life for NDMA has been measured for about three weeks in aerobic soil under laboratory conditions (HSDB, 2003b).

Health Effects.

Exposure to high levels of NDMA may cause liver damage in humans. Symptoms of overexposure include headache, fever, nausea, jaundice, vomiting, and dizziness (ATSDR, 1999; HSDB, 2003b). NDMA is classified as a B2 carcinogen – reasonably anticipated to be a human carcinogen (ATSDR, 1999; USEPA IRIS, 2009).

N-nitroso-di-n-butylamine

Properties and Sources. N-nitroso-di-n-butylamine (NDBA) is pale yellow oil with a characteristic odor. It is miscible with hexane, dichloromethane, and many other organic solvents. The vapor pressure is $4.69 \mathrm{X} 10^{-2}$ mm Hg at 25°C. Estimated adsorption coefficient (Koc) is 642 (log Kow of 2.63). The estimated Henry's Law constant is $1.32X10^{-5}$ atm-cu m/mol (ChemIDPlus, 2004c). When heated to decomposition, NDBA emits toxic fumes of nitrogen oxides (NO_x). NDBA is used primarily as a research chemical (IARC, 1974). It has also been used as an intermediate in the synthesis of di-n-butylhydrazine (NTP, 2011). In addition, NDBA has been formed as a waste product at rubber manufacturing plants and factories that use metal working fluids may release to the environment (HSDB, 2003c).

Environmental fate and behavior. NDBA contamination may be found in air, water and soil. Environmental releases of NDBA since 1998 have been to landfills. Annual releases did not exceed 15 lb from 1998 through 2000 or in 2004, but were 4,510 lb in 2001. In 2007, a facility released 500 lb of NDBA to an off-site hazardous-waste landfill (TRI, 2012c).

Air -- The vapor pressure measurement estimates NDBA will exist as a vapor in the ambient atmosphere. Vapor-phase NDBA will be degraded in the atmosphere by photochemical reactions that produced hydroxyl radicals. This half-life is very short and is estimated at 1.4 hours. Photolysis half-live measured at various pHs ranged from 16 minutes to 3.6 hours (HSDB, 2003c).

Water -- NDBA may adsorb to suspended solids and sediment based upon the estimated Koc. Due to the Henry's Law constant, volatilization from water surfaces is expected. Estimated volatilization half-lives for a model river and model lake are 2.4 days and 30 days, respectively (HSDB, 2003c). NDBA may biodegrade in water based on the biodegradation of the chemical structure N-nitrosodi-n-propylamine (NDPA) which is a similar structure (HSDB, 2003c).

Soil – The estimated Koc value means NDBA is expected to have low mobility. Volatilization from moist soil surfaces is expected based upon the estimated Henry's Law constant. However, volatilization is not expected from dry soil surfaces. NDBA may biodegrade in soil based on a soil mineralization half-life of 7 days due to its structure which is similar to NDPA (HSDB, 2003c).

Health Effects. NDBA caused tumors in several species of experimental animals, at several different tissue sites, and by several different routes of exposure. No epidemiological studies were identified that evaluated the relationship between human cancer and exposure specifically to NDBA. NDBA is reasonably anticipated to be a human carcinogen based on sufficient evidence of carcinogenicity from studies in experimental animals (IARC, 1978)(NTP, 2011).

N-nitroso-di-n-propylamine

Properties and Sources. N-nitroso-di-n-propylamine (NDPA) is a yellow liquid with no characteristic odor. It is soluble in water, lipids, and organic solvents. It is stable in the dark in neutral or alkaline solution for at least 14 days, but is less stable in more acidic solutions or in light, especially ultraviolet light (IARC 1978). The vapor pressure is 0.086 mm Hg at 20 °C. The estimated adsorption coefficient (Koc) is 130 (log Kow of -0.57). The estimated Henry's Law constant is $5.38X10^{-6}$ atm-cu m/mole (ChemIDPlus, 2004d). It has been identified as a contaminant in dinitrotrifluralin herbicides, and thus may be released to the environment when these herbicides are used and from spills. NDPA has been detected in extruded rubber products, cheese, and alcoholic beverages, and in the herbicides trifluralin, isopropalin, and oryzalin at low concentrations (17 to 190 ppm) (IARC, 1978, ATSDR ,1999c, HSDB, 2003b). NDPA is used in small quantities in laboratory research. It has no known commercial use (IARC, 1978, ATSDR, 1989, HSDB, 2009).

Environmental fate and behavior. Low levels of NDPA could be released to the environment from contaminated products or from disposal of waste containing this chemical. In 1998, two facilities released a total of 2,379 lb of NDPA to the environment and one facility released 5 lb in 1999. Since 2001, releases have ranged from a low of 257 lb in 2002 to a high of 755 lb in 2005. In 2007, 250 lb was released to air and 500 lb to an off-site hazardous-waste landfill (TRI, 2012d).

Air – The vapor pressure measured estimates NDPA as a vapor in the ambient atmosphere. Vapor-phase NDPA is degraded in the atmosphere by reaction with photochemically that produced hydroxyl radicals. The photochemical reaction had a half-life for this reaction in air is estimated to be 16 hours. However, the use of a photoreactor, half-life was determined to be 5 to 7 hours (HSDB, 2009).

Water -- NDPA will not adsorb to suspended solids and sediment based upon the estimated Koc. Due to the estimated Henry's Law constant, NDPA is expected to volatilize slowly from water surfaces. Estimated volatilization half-lives from a model river and model lake are 7.9 and 61 days, respectively. The half-life is calculated to occur in 8 hours due to degradation in surface water due to photolysis.

Soil – A high mobility in soil is expected due the estimated Koc value. A large portion of NDPA will rapidly volatilize if released onto the soil surface. NDPA readily photolyzes and would be expected to photolyze on the soil surface. Experiments found 50% of NDPA was lost in 6 hours when applied to the soil surface, but when mixed into soil, volatilization is prolonged and significantly reduced. Other experiments found only 6% volatilized in 8 days when mixed into soil at a depth of 7.5 cm. NDPA's half-life in aerobic soils under laboratory conditions was about 3 weeks with volatilization and biodegradation the primary removal processes.

Health Effects. NDPA caused tumors in two rodent species, at several different tissue sites, and by two different routes of exposure. In rats, it caused liver cancer (hepatocellular carcinoma) and benign and malignant tumors of the esophagus (papilloma and carcinoma) following administration in the drinking water or subcutaneous injection (IARC, 1978). Subcutaneous injection of NDPA also caused tumors of the lung and nasal and paranasal cavities in hamsters and rats, tumors of the laryngobronchial tract in hamsters, and benign and malignant kidney tumors (adenoma and adenocarcinoma) in rats.

No epidemiological studies were identified that evaluated the relationship between human cancer and exposure specifically to NDPA. NDPA is reasonably anticipated to be a human carcinogen based on sufficient evidence of carcinogenicity from studies in experimental animals (ATSDR, 1999; USEPA IRIS, 2009).

N-nitroso-methylethylamine

Properties and Sources. N-nitroso-methylethylamine (NMEA) is a yellow liquid with no characteristic odor. There is insufficient data available and most data is based on nitrosamines in general. It is soluble in water, lipids, and organic solvents. The vapor pressure is 1.1 mm Hg at 20 °C. The estimated adsorption coefficient (Koc) value is 25 (log Kow 0.04). The estimated Henry's Law constant is $1.44X10^{-6}$ atm-cu m/mol (ChemIDPlus, 2004e). NDBA is used primarily as a research chemical (IARC, 1978).

Environmental fate and behavior. It may be formed in the atmosphere by reaction with atmospheric amines and nitrous acid. NMEA may be released to the environment in tobacco smoke. No releases were documented in USEPA's TRI database.

Air -- The vapor pressure measurement estimates NMEA will exist as a vapor in the ambient atmosphere. The half-life is calculated to be 5.8 minutes and 1.6 days due to degradation in the atmosphere with direct photolysis and by reaction with photochemically produced hydroxyl radicals, respectively.

Water -- NDBA is not expected to adsorp to suspended solids and sediment in the water column due to the estimated Koc. Volatilization of NMEA from water surfaces is expected to occur based upon this compound's estimated Henry's Law constant. Estimated volatilization half-lives from a model river and a model lake are 24 and 180 days, respectively.

Soil -- The estimated Koc value also indicates NMEA is expected to have high mobility. The estimated vapor pressure indicates this compound may potentially volatilize from dry soil surfaces. An estimated Henry's Law constant indicates volatilization from wet soil surfaces is expected.

Health Effects. NMEA is a carcinogenic in several animal studies. Rats developed liver tumors in addition to esophageal carcinoma. In rats, it caused liver cancer (hepatocellular carcinoma), benign and malignant tumors of the esophagus (papilloma and carcinoma), lung metastases, and leukemia following administration in the drinking water or subcutaneous injection (IRIS, 1993d).

No epidemiological studies were identified that evaluated the relationship between human cancer and exposure specifically to NMEA. NMEA is reasonably anticipated to be a human carcinogen based on sufficient evidence of carcinogenicity from studies in experimental animals (ATSDR, 1999; USEPA IRIS, 2009).

N-nitroso-pyrrolidine

Properties and Sources. N-nitroso-pyrrolidine (NPYR) is a yellow liquid with no characteristic odor. It is totally soluble in water, organic liquids, and lipids. The vapor pressure is $6.0X10^{-2}$ mm Hg at 20 °C. Estimated adsorption coefficient (Koc) is 19 (log Kow of -0.19). The estimated Henry’s Law constant is $4.89X10^{-8}$ atm-cu m/mole (ChemIDPlus, 2004f). NPYR is stable at room temperature in the dark, but is sensitive to light, especially ultraviolet light (IARC, 1978). NPYR is used primarily as a research chemical and is not produced commercially in the United States (IARC 1978, HSDB 2003d). NPYR is formed by the reaction of pyrrolidine with potassium nitrate in a weak hydrochloric acid solution. The heating of pyrrolidine at 185-200 °C causes NPYR to form.

Environmental fate and behavior. NPYR may be released to the environment from cigarette smoke, bacon frying, wastewater discharges, rubber tire production, and sewage sludge. No releases were documented in USEPA's TRI database.

Air – The vapor pressure measurement estimates NPYR will exist as a vapor in the ambient atmosphere. The half-life is estimated to be 20 hours when vapor-phase reacts with photochemically that produced hydroxyl radicals.

Water -- NPYR is not expected to adsorb to suspended solids and sediment in the water column. Volatilization from water surfaces is not expected to occur based upon this compound's measured Henry's Law constant.

Soil -- The estimated Koc value also indicates that NPYR is expected to have very high mobility in soil. The importance of biodegradation is unknown. Volatilization from wet and dry soil surfaces is not expected due to NPYR Henry's Law constant and vapor pressure.

Health Effects. NMEA is carcinogenic in several animal studies where various animals developed liver tumors. In rats, it caused liver cancer (hepatocellular carcinoma), benign tumors of the lungs (adenoma), lung metastases and leukemia following administration in the drinking water or subcutaneous injection (IARC, 1978). Hamsters developed tumors of the larynx or trachea and preneoplastic and neoplastic nasal-cavity lesions. (IRIS, 1993e)

No epidemiological studies were identified that evaluated the relationship between human cancer and exposure specifically to NPYR. NPYR is reasonably anticipated to be a human carcinogen based on sufficient evidence of carcinogenicity from studies in experimental animals (ATSDR, 1999; USEPA IRIS, 2009).

Table 1

Six nitrosamines with CAS number and uses

Compound	**CAS**	**Uses**
N-nitroso-diethylamine (NDEA)	55-18-5	An additive in gasoline and in lubricants, an antioxidant, and a stabilizer in plastics
N-nitroso-dimethylamine (NDMA)	62-75-9	Once used in the production of rocket fuels, used as an industrial solvent and an anti-oxidant
N-nitroso-di-n-butylamine (NDBA)	924-16-3	Research chemical
N-nitroso-di-n-propylamine (NDPA)	621-64-7	Research chemical
N-nitroso-methylethylamine (NMEA)	10595-95-6	Research chemical
N-nitroso-pyrrolidine (NPYR)	930-55-2	Research chemical

Source: USEPA CCL3 List

Note: CAS is a division of the American Chemical Society, which provides chemical information and unique identifiers for chemical substances.

Table 2

Six nitrosamines chemical properties

Compound	**Mass**	**Formula**	**BP (°C)**	**FP (°C)**	**Density (g/cm^3)**
NDEA	102.14	$C_4H_{10}N_2O$	177	62	0.95
NDMA	74.08	$C_2H_6N_2O$	153	142	1.005
NDBA	158.142	$C_8H_{18}N_2O$	250.6	No Data	0.91
NDPA	130.111	$C_6H_{14}N_2O$	113	10	0.92
NMEA	88.10932	$C_3H_8N_2O$	163	No Data	0.94
NPYR	100.2	$C_4H_8N_2O$	214	182	1.085

Source: ChemIDPlus 2004

Note: g/cm3 - density of water is one gram per cubic centimeter

Previous Occurrences

Several studies have found nitrosamine in surface water and ground water, in addition to drinking water. These studies were conducted in the US, Canada and Japan however nitrosamines appear to be a concern for the US and Canada.

US and Canada

American Water Works Association Research Foundation (AWWA) and Water Environment Research Foundation jointly funded a study from 2001 to 2002 that focused on NDMA occurrence in seven states and four Canadian provinces drinking water treatment plants. Water sampling was taken from 21 water treatment facilities at 3 sampling sites; treatment plant influent, finished water, and distribution system were analyzed for NDMA (Barret et al., 2003). Most NDMA analyses were performed by solid-phase extraction with a carbon resin and gas chromatography. NDMA in raw waters were below detection limits. However, concentrations of NDMA were detected in chloraminated waters. The detection level was found to be slightly higher than the chlorinated waters. The study also confirmed NDMA formation is relatively slow when chloramine is part of the treatment chain. The median NDMA concentration was less than 2 ng/L in a chloraminated drinking water distribution system and less than 1 ng/L in a chlorinated one. The concentration of nitrosamine increased with distance from the treatment plant.

Canada

In 1989, NDMA was first discovered in treated drinking water in Ontario, Canada (OME, 1994). NDMA was added to Ontario's Drinking Water Surveillance Program (DWSP) in 1994, which consisted of a list of contaminants for its occurrence survey. Charrois et al. have surveyed 179 Ontario water treatment plants during 1994-2002. The study focused on influent, effluent, and distribution water samples and analyzed over 3,000 samples.

Concentrations in effluents from drinking water treatment plants using chlorine as a disinfectant showed median NDMA concentrations were less than 1 ng/L, while effluents from plants using chloramines and their distribution systems showed median NDMA levels of 1.3 ng/L and 2.2 ng/L, respectively. More than 58% of effluent or distribution system samples disinfected by chlorine showed NDMA concentrations of less than ~1 ng/L; however, NDMA concentrations up to 66 ng/L was observed in some of the distribution system samples. In addition, NDMA concentrations up to 65 ng/L for effluent samples treated by chloramines were observed.

This study confirmed that some raw waters may already contain NDMA and that both chlorination and chloramination of waters may cause the formation of nitrosamine. Although chlorination may produce some NDMA, the median concentration values of chlorinated systems were low. For chloraminated systems, median NDMA concentrations were slightly higher than the chlorinated systems for effluent and distribution samples. NDMA was detected in 30% of the samples and very small quantities of N-nitroso-morpholine and NPYR have been detected in some waters. In addition, NDMA concentrations were associated with facilities that use chloramine for final disinfection. According to Charrois et al. , the detection of nitrosamines in water may be positively correlated with the presence of organic nitrogen.

California

In 1998, at Baldwin Park in Rancho Cordova and in the San Gabriel Valley, NDMA in liquid rocket fuels was discovered to be the source of contamination of groundwater (California Department of Health Services [CDHS], 2002). In Rancho Cordova the concentrations of NDMA in groundwater onsite were up to 40,000 ng/L, and offsite up to 20,000 ng/L (Mitch et al., 2003). In San Gabriel Valley, which is downgradient of the rocket engine testing facility, concentrations of NDMA were found up to 3,000 ng/L. Three drinking water wells were impacted; two wells were closed and the third was already closed due contamination of NDMA and another compound.

Due to these findings, the California Department of Health Services conducted a survey of nitrosamines in 32 water treatment plants in 2001 (CDHS, 2002). The survey confirmed the detection of NDMA in some raw waters. In 3 of 20 chloraminated drinking water supplies, NDMA concentrations exceeded 0.01 μg/L, whereas all 8 supplies that used only free chlorine had levels below 0.005 μg/L.

This study indicated that chloramination is an important source of NDMA. However, the study also showed that the raw water contains precursors that react with chloramine to produce nitrosamine. No correlation was found for the following possible factors: chlorine residual (both free and total), pH, temperature, alkalinity, total organic carbon, nitrate, nitrite, ammonia, and total nitrogen.

Japan

A survey of NDMA occurrence was completed in raw and finished waters from many water treatment plants (Huy et al., 2011). The objective of the research was to determine the extent of the occurrence of NDMA in ground water, evaluate the formation by chlorination and chloramination; and research the factors that cause the NDMA formation (Huy et al., 2011).

The sampling was conducted from September to October 2007 and December 2007 to January 2008. There were 59 samples taken and 24 sample detects for NDMA. NDMA was detected in raw waters in concentrations up to 4.3 ng/l. The NDMA concentrations were greater in waters containing higher levels of total nitrogen. NDMA was detected in the finished water with concentrations up 10 ng/l (Huy et al., 2011).

Sampling and Analytical Techniques

Occurrence of nitrosamines in water is determined by a variety of methods as well as the detection level. Some studies rely on liquid-liquid extraction or solid-phase extraction. Charrois et al stated some analytical methods are inadequate at low ng/l concentrations due to inefficient extractions. There is a need for selective and sensitive analytical methods (Charrois, 2004). Charrois et al used a positive chemical ionization with ammonia reagent gas. In addition, there is a study that was completed in Korea, where the analysis of water samples for nitrosamines using high performance liquid method chromatography with fluorescence detection (Hekap, 2011; Charrois, 2007). This method was developed by Cha et al from Arizona State University for aqueous determination of NDMA (Cha et al., 2006).

The detection of N-nitrosamines as NDMA, NMEA, and NDEA in water is very difficult, because these compounds are found in water at concentrations of a few ng/L due to the low maximum acceptable concentration in water. USEPA had standard methods available, such as Test Methods for Evaluating Solid Waste, Physical/Chemical Methods (SW 846). SW 846 methods include 8070 and 8270; the former is not routine, and the latter has a high detection limit relative to the risk level. However, unless nitrosamines (e.g. NDMA) are present at a relatively high concentration, NDMA would not likely be detected under routine Gas chromatography (GC) or GC/mass spectrometry (MS) scans.

Nitrosamine Analytical Challenges

Nitrosamines are miscible with water in all proportions, making solvent extraction difficult and inefficient. However, the use of solid phase extraction (SPE) using carbon provides better extraction efficiency. There is low response with electron ionization (EI) MS and conventional GC detectors. GC/MS or GC/MS/MS is used for specificity by using methanol chemical ionization (CI) for better sensitivity. Low detection limit are needed due to health effects data. Therefore, large volume injection is used to enhance sensitivity. USEPA developed and requires laboratories to use the Analytical Method 521, which uses the solid phase extraction and capillary column gas chromatography with large volume injection and chemical ionization tandem mass spectrometry. (Munch & Bassett, 2007)

Method 521

Method 521 is a procedure using activated carbon for the determination of various nitrosamines in finished drinking water. The method can also be used for untreated source waters but has not been evaluated for these sources. Nitrosamines are thermally stable and volatile for direct analysis by gas chromatography.

Analytes and surrogates are extracted when a 500 mL water sample is drawn through a solid phase extraction cartridge containing 2 grams of coconut-activated carbon. The organic compounds are eluted from the solid-phase with a small quantity of methylene chloride. The solvent is concentrated and an internal standard added. The sample components are identified after injection on a fused silica capillary column of a GC/MS/MS equipped with a large volume injection injector.

Interferences

Analyses of laboratory reagent blanks provide information about the presence of contaminants. Nitrosamines may be present in trace amount in rubber products, such as gloves and water systems. Rubber-coated septa on injection vials may also introduce nitrosamines into the sample which would give false detection levels. During analysis, major contaminant sources that affect sampling results are reagents and SPE devices. Solid phase extraction devices described in the 521 method have two potential sources of contamination-both the solid phase sorbent and the polypropylene cartridge that it is packed in. NDMA can leach from rubber products; therefore it is recommended that water stored in glass bottles have PTFE caps.

Sample Collection

- Field sampling equipment must be free of plastic or rubber tubing
- All field samples must be dechlorinated with 80-100 mg of sodium thiosulfate per liter at time of collection
- Samples must be iced during shipment and not exceed 10°C
- Samples stored in the lab must be held at 6ºC
- Analyze within 14 days after collection
- Sample extracts can be stored up to 28 days in amber vials at -15°C or less and protected from light

Chapter 3

METHODOLOGY

Sources used in this study include literature reviews of journal articles, and government documents. In addition, the collection and analysis of secondary data gathered from USEPA, and public water systems based on the UCMR 2 are sources.

Data Analysis

1. Analyzed the extent of occurrence of the nitrosamine in drinking water
2. Analyze the extent of occurrence based on disinfectants (chlorine or chloramines) used for treatment and water sources (ground water or surface water)

Occurrence of Contamination

The study requires the evaluation of known occurrence in PWSs using UCMR 2 data. Is the contaminant known or likely to occur in PWSs at a frequency and level of public health concern? The data from several occurrence data sets were analyzed to develop representative occurrence estimates for public drinking water systems. This was completed by the presenting the data by water type, system size and state. This analysis will focus on disinfection by-products known as N-nitroso-diethylamine (NDEA), N-nitroso-dimethylamine (NDMA), N-nitroso-di-n-propylamine (NDPA), and N-nitroso-pyrrolidine (NPYR). In addition, N-nitroso-di-n-butylamine (NDBA), N-nitroso-methylethylamine (NMEA), monitored as part of the screening survey.

Sampling Data

The UCMR 2 data set used for this study required monitoring for 25 contaminants using five analytical methods during 2008-2010. This research will focus only on the six nitrosamines analyzed using EPA method 521. UCMR 2.

Screening survey monitoring uses specialized analytical method technologies not commonly used by drinking water laboratories. The UCMR 2 representative data design is that all PWSs serving more than 100,000 people, 320 representative PWSs serving 10,001-100,000 people, and 480 representative PWSs serving less than 10,001 people are required to monitor for the 15 “List 2” contaminants which included the four disinfection by-products known as NDEA, NDMA, NDPA, and NPYR. In addition, NDBA and NMEA were added and collected during the UCMR 2.

The occurrence data from the UCMR 2 was retrieved in April 2011, July 2011, and January 2012, from U.S. EPA website located at http://water.epa.gov/lawsregs/rulesregs/sdwa/ucmr/data.cfm which is stored in NCOD. I used Excel pivot tables to extrapolate and present the data in several ways for each nitrosamine contaminant to characterize various aspect of occurrence.

Statistical analysis of the UCMR 2 data consists of simple counts and statistics of analytical occurrence data for each of the six nitrosamine contaminants. These occurrence analyses are conducted at the level of samples, sample points, systems, and population served. At the sample level, occurrence measures include: the number and percent of samples for each contaminant with analytical detections, and the minimum, median, maximum, and 99th percentile values of those detections. System-level occurrence measures include: the number and percent of systems with one or more analytical detections.

In addition, the simple counts are made of the number of systems, and populations served by those systems, with at least one result above a specified concentration threshold. Any of the six contaminants results found to have significant occurrences at or near health reference level (HRL) concentrations would be at a level of public health concern.

The population and basic inventory data was retrieved from USEPA website located at http://water.epa.gov/scitech/datait/databases/drink/ sdwisfed/ howtoaccessdata.cfm. Population served occurrence measures include: the number and percent of customers (population served) by systems with one or more analytical detections, and the number of a given contaminant. For analysis of UCMR 2 data, the following source water type is treating mixed water sources (Mx), ground water under the influence of surface water (GU), and purchased surface water (SWP) as surface water.

Chapter 4

RESULTS

UCMR data analysis

This section discusses the results from the analyses of the UCMR data. The data results from the UCMR databases described in Chapter 3 were collected from January 2008 – December 2010 (Figure 10). All systems serving more than 100,000 people and 800 systems serving less than 100,001 people were required to sample for the UCMR 2.

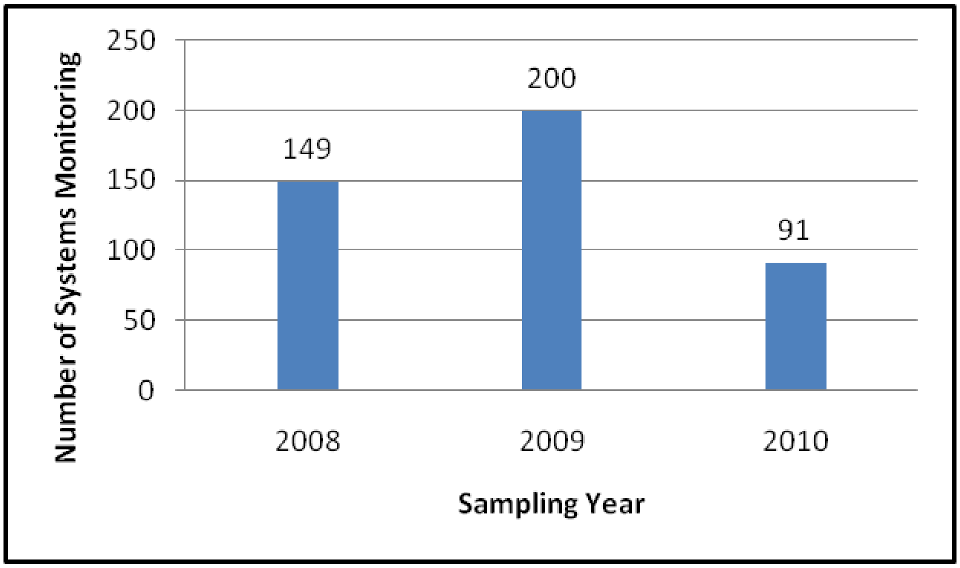

Figure 10. Number of PWSs collecting UCMR 2 Samples Each Year (2008-2010)

List 2 contaminants were scheduled to be monitored by 1,200 public water systems. Eighty-eighty percent of small systems in the data set were community water system (CWS). In the large system census, more than 99% of systems are CWSs, only 1% were transit non-community water systems (TNCWSs), as there were no large Non-transit community water systems (NTNCWS). This distribution represents the various water treatment needed based on population served (Appendix – Table A-1).

The number of public water systems monitoring in UCMR 2 by source water type and system size is shown in Table 3. The representative sample design is based on the UCMR 2 which is based on system size (population served), source of water type (ground water or surface water), and geographic location (state or territory). This distribution represents the various types of water treatment based on disinfectant used (chlorine or chloramines) needed based on system size and source water type (Appendix – Table A-2 and A-3).

The system size determines how many consumers are affected by the quality of the drinking water. The source water determines the possible precursors and water treatment that is needed.

Table 3
Number of public water systems by source water type and system size

Water Type	VS	S	M	L	VL	XL	Total
GUDI	7	2	5	2	0	5	21
GW	81	83	88	90	83	98	523
MX	0	2	1	8	7	29	47
SW	72	73	66	60	70	266	607
Total	160	160	160	160	160	398	1198

Note: Ground water under the direct influence (GUDI) of surface water; ground water (GW); Mix of ground water and surface water (MX) and surface water (SW). The dataset is missing for two public water systems for the expected 1200 PWS to participate; very small (VS), small (S), medium (M), large (L), very large (VL), extra large (XL).

This study used the UCMR 2 data set (UCMR 2, 2012) for nitrosamines only, the January 2012 version was used for this analysis, which contains 108,604 individual sample analytical results for the six contaminants, including 1,960 sample detections for five (NDEA, NDMA, NPYR, NDBA, and NMEA) of the CCL 3 contaminants monitored under the UCMR 2. The data set included the following inventory information for each sampling site:

- Public water system identification (PWS ID): the code used to identify each PWS
- PWS name:
- PWS facility identification: an identification code given by the state
- PWS facility name: defines the facility, such as treatment plant
- Size: the system size is based on population served

- Facility water source type: defines where the facility is retrieving their water (lake, river (SW) or ground water, etc.)
- Sample point identification: defines each sampling point
- Sample point type: an identification of the sampling location
- Disinfectant residual: the type of disinfectant used

The monitoring schedules for these systems were spread over a period of time to ensure that results were collected from every month in every part of the country. In this way, the UCMR 2 results reflect multiple seasons and multiple years of climatic conditions throughout the country and are not directly affected (or biased) by weather conditions of a single season, year, or geographic region. There were at least one or more detections of at least one of the six nitrosamines in 48 states (Appendix-Table A-4). Ground water systems were required to sample two times, 5 to 7 months apart within a 12-month period. Surface water and groundwater mixed with surface water or GUDI systems were required to sample four times within a 12-month period in which each sample was required to be taken 3 months apart. The distribution in Table A-4 shows the analytical samples taken by system size and source water type (Appendix-Table A-5).

The data presented in this report providing a summary of occurrence information on all six UCMR 2 contaminants, are presented in the Appendix - Tables A-6-9. The breakdown of the nitrosamines occurrence data is by system size and by source water type. There were no correlations of occurrence with system size as noted with source water type (SW, GW etc.). The data has been analyzed at the level of detection at or above the MRL per each nitrosamine

(Table 4). MRL is an estimate of the lowest concentration of a compound that can be quantitatively measured. The MRLs are based on Lowest Concentration Minimum Reporting Levels (LCMRLs) which represent the lowest concentration of a compound that can be quantitatively determined. Only one out of the six contaminants (NDPA) had no analytical detections in any of the water systems that were sampled under the UCMR 2. The other five contaminants had multiple detections in water systems.

According to the UCMR program, if the Health Reference Level (HRL) is less than the MRL, the data is not analyzed at the level of the HRL or half the HRL. Health reference levels refer to exposure levels that will not cause significant risks of non-cancer health effects. Most nitrosamines are classified as probable human carcinogens because of laboratory animal experiments.

Detection Occurrence in UCMR 2

The frequency of nitrosamine occurrence in the UCMR 2 is similar to results reported by Russell et al, 2012. The study used the data as of October 1, 2010 and focused on the community water systems. In addition, this study analyzed nitrosamine occurrence in Ontario for comparison with UCMR 2 data. The raw data was reported in micrograms per liter (ug/L) which was converted to nanograms per liter (ng/L) units.

Table 4

Summary Occurrence Measures – Detections

Compounds	MRL (ng/L)	# Samples With Detection	# Systems With Detection	Population Served with Detection
NDEA	5	46	26	~13M
NDMA	2	1861	324	~94M
NDBA	4	9	5	~2M
NDPA	7	0	0	0
NMEA	3	3	3	~0.2M
NPYR	2	41	21	~9M

Note: Under UCMR 2, total population served is the sum of the direct retail population served plus the population served, if any, by any consecutive system(s) receiving its finished water from the wholesaler PWS. Stage 2 DBPR defines a consecutive system as a PWS that receives some or all of its finished water from one or more wholesale systems. Finished water is defined as water used in the distribution system and intended for distribution and consumption without further treatment (except treatment as needed to retain water quality in the distribution system, such as booster disinfection or addition of corrosion control chemicals).

NDEA. The 26 public water systems that detected NDEA in UCMR 2 comprised 2% of all the systems that performed the sampling. The 46 detections in these 26 PWSs comprised 0.3% of NDEA. The NDEA concentrations ranged from 5 – 100 ng/L, and the median and average concentration was 7 ng/L and 15 ng/L, respectively. The HRL for NDEA is 0.2 ng/L, which is less than the MRL, therefore HRL is not calculated. (Appendix A, Table A-10)

NDEA was detected in 9 states, which included California with 154 PWS, comprising 43% of all the systems with detections. These included 14 PWSs with 22 detections (48% of the detections nationwide) of which 4 detections were above California's notification level. There were no differences in detection concentrations based on source water type (SW or GW), 0.3% and 0.2%, respectively (Appendix A, Tables A-10-17).

NDMA. The 324 public water systems that detected NDMA in UCMR 2 comprised 27% of all the systems that performed the sampling. The 1,861 detections comprised 10% of NDMA analyses. NDMA concentration ranged from 2 - 630 ng/L, and the median and average detection level was 4 ng/L and 9 ng/L, respectively. The HRL for NDMA is 0.7 ng/L, which is less than the MRL, therefore HRL is not used (Appendix A, Table A-17).

NDMA was detected in 45 states and/territory, which included California with 154 PWS comprising 14% of all the systems with detections. These included 69 PWSs with 491 detections (which is 26% of the detections nationwide), 32 detections were above California's notification level of 10 ng/L. In addition, including Texas with 117 PWS comprising 10% of all the systems that performed the sampling. These included 64 PWSs with 583 detections (which is 31% of the detections nationwide). Although, Texas has not determined a MCL or notification level for nitrosamine, 220 detections were above California's notification level. NDMA is found to be the predominant nitrosamine in drinking water systems. NDMA was detected three times more frequently in SW than GW. ―the most frequently detected with the highest concentrations (Appendix A, Tables A-18-22).

NDBA. The 5 public water systems that detected NDBA in UCMR 2 comprised 0.4% of all the systems that performed the sampling. The 9 detections comprised 0.0% of NDBA analyses. NDBA concentration ranged from 4 - 21 ng/L; and the median and average detection level was 7 ng/L and 8 ng/L. The HRL for NDBA is 6 ng/L, 6 PWS were above HRL. However the ½ HRL is less than the MRL, therefore ½ HRL is the not used. (Appendix A, Table A-23)

NDBA was detected in 4 states, which included California with 154 PWS comprising 63% of all the systems with detections. These included 2 PWSs with 3 detections (which is 33% of the detections). NDBA was only detected in GW (Appendix A, Tables A-24-28).

NMEA. The 3 public water systems that detected NMEA in UCMR 2 comprised 0.3% of all the systems that performed the sampling. The 3 detections comprised 0.0% of analyses. NMEA concentration ranged from 4-5 ng/L; and the median and average detection level was 4 ng/L and 4 ng/L. The HRL for NMEA is 2 ng/L, which is less than the MRL, therefore HRL is the not used (Appendix A, Table A-29).

NMEA was detected in 2 states, which included Oklahoma with 19 PWS comprising 40% of the systems with detections. These included 2 PWSs with 3 detections (which is 67% of the detections). In addition, including Washington with 29 PWS comprising 60% of the systems with detections. This included a

PWS with a detection (which is 33% of the detections). NDBA was only detected in SW (Appendix A, Tables A-30-34).

NPYR. The 21 public water systems that detected NPYR in UCMR 2 comprised 2% of all the systems that performed the sampling. The 41 detections comprised 0.2% of NPYR analyses. NPYR concentration ranged from 2 - 24 ng/L, and the median and average detection level was 4 ng/L and 5 ng/L, respectively. The HRL for NPYR is 20 ng/L, 2 PWS > HRL and 1 PWS > ½ HRL (Appendix A, Table A-35).

NPYR was detected in 11 states, which includes Texas with 96 PWS comprised 40% of the systems with detections. These included 2 PWSs with 3 detections (which is 67% of the detections). In addition, including Washington with 29 PWS comprised of 60% of the systems with detections. This included a PWS with a detection which comprised 33% of the detections. It is worth noting, although California had detections, it was rather small. NPYR was only detected in SW (Appendix A, Tables A-36-40).

NDMA detections higher compared to the other nitrosamines is consistent with the literature reviews (Mitch et al., 2003). Although detection frequencies vary significantly among the five detected nitrosamines, overall the mean concentrations for the samples with detections results were similar, ranging from 4 to 15 ng/L for UCMR 2 samples (Russell et al., 2012).

California and Texas accounts for 56% of the detections, in which California water quality concerns is well documented (CDHS, 2004). According to the 2010 Texas Integrated Report, which describes the status of Texas' natural waters based on historical data. Texas is well known for petroleum refineries and agriculture. The most common contaminants reported in 2008 included gasoline, diesel, and other petroleum products, due to the large number of petroleum storage tank. The 2010 groundwater inventory shows that ambient groundwater quality in Texas had MCL exceedances occurring for some nitrate contaminants (Texas Commission on Environmental Quality (TCEQ), 2010). Nitrosamine has been shown as a product or released into the environment from industrial sources and from chemical reactions with nitrate (ASTDR, 1989).

Occurrence based on disinfectants used and sampling point

USEPA required nitrosamines to be measured at two locations to provide an understanding of the proportion of nitrosamines, particularly NDMA, that result from source water contamination versus that which results from disinfection. Samples were collected at the entry point to the distribution system (EPTDS) for all List 2 contaminants. For those systems that utilize chemical disinfection, additional samples were collected for nitrosamines using EPA Method 521.0 at the distribution system maximum residence time (DSMRT) sampling point associated with each plant/water source, as defined in the Stage 1 DBP.

Public water systems that submitted data for disinfection type indicated that they use chloramines, chlorine, other, or they did not make a selection (Table 5). There were 496 PWSs selected chlorine and 218 PWSs selected chloramines as a disinfectant. Nitrosamine detection was more frequent with water systems using chloramines versus chlorine. It is worth noting that in GW systems without disinfection treatment, essentially no nitrosamine was detected. Chloramines are often used in place of chlorine because they are known to produce less chlorinated DBPs. However, chloramines appear to be linked to increasing the production of nitrosamines. These results are consistent with previous studies that have shown the importance of NDMA formation with drinking water systems using chloramines (Schreiber & Mitch, 2006; Choi & Valentine, 2002; Mitch & Sedlak, 2002).

Table 5

Summary Occurrence Measures – Detections by Disinfectant Type

Compounds	# Samples w/ Detection	Chlorine	Chloramines	Others or Unknown
NDEA	46	27	9	10
NDMA	1861	296	1008	557
NDBA	9	9	0	0
NDPA	0	0	0	0
NMEA	3	3	0	0
NPYR	41	14	24	3

The water systems with NDMA detections that used disinfectant with chlorine and chloramines with concentrations up to 85 ng/L and 630 ng/L, respectively. The surface water systems with NDMA detections that used chlorine had 91 detections at the EPTDS; the median and average concentration was 4.7 ng/L and 4 ng/L, respectively. The maximum level was 61.7 ng/L. There were 120 detections at the DSMRT; the median and average detection level was 4.2 ng/L and 7.9 ng/L, respectively. The surface water systems with NDMA detections that used chloramines had 367 detections at the EPTDS; the median and average concentration was 7.0 ng/L and 9.3 ng/L, respectively. The maximum level was 470 ng/L. There were 581 detections at the DSMRT; the median and average concentration was 7.8 ng/L and 9.8 ng/L, respectively.

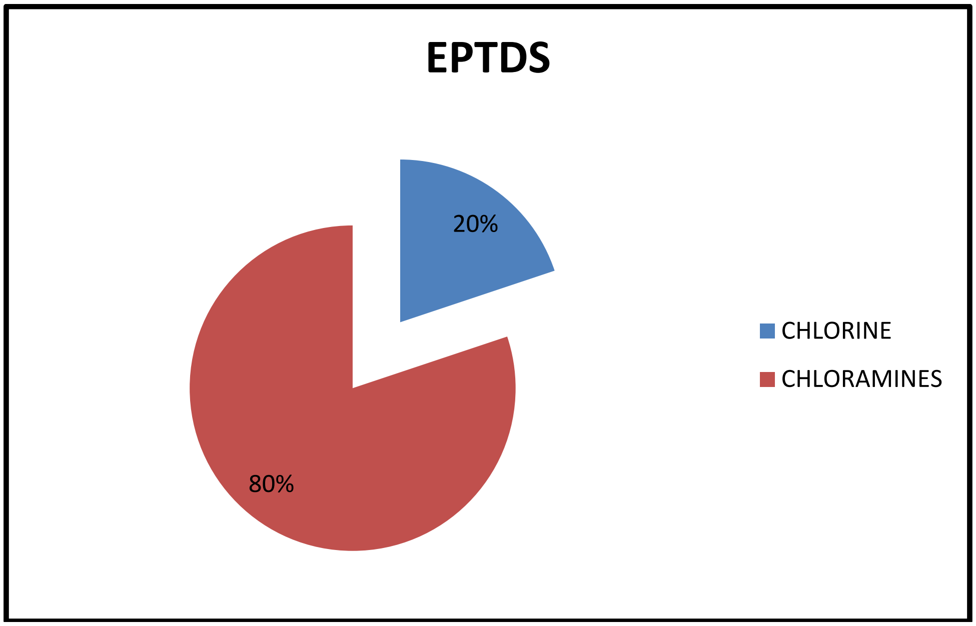

Figure 11. Percentage of detections based on disinfectant used at the entry point

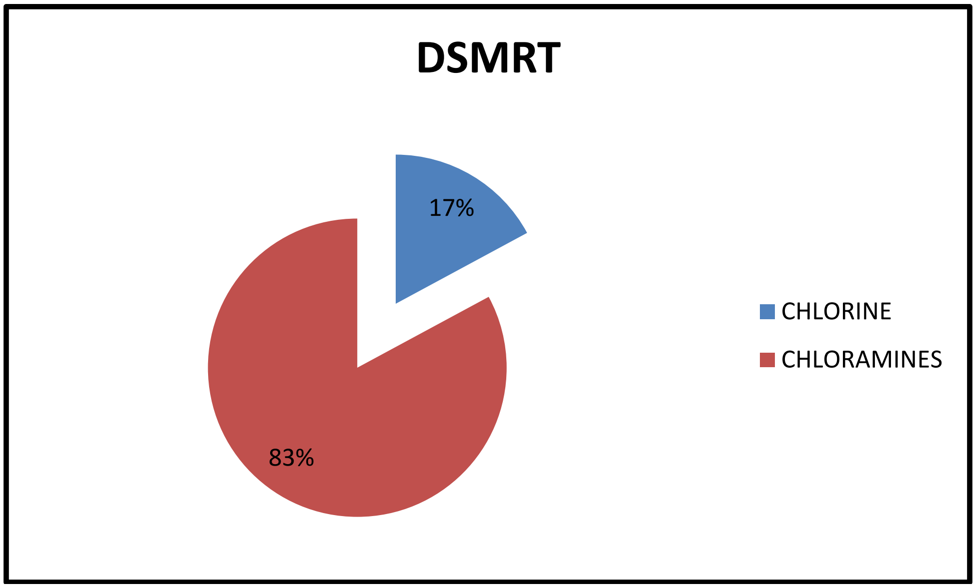

Figure 12. Percentage of detections based on disinfectant used at the maximum residence time

Figures 11 and 12 shows two thirds of the detections above the MRL occurred at water systems that used chloramines. The higher detections at the maximum residence time support previous studies where NDMA is expected to be higher. As discussed in Chapter 2, nitrosamines increased due to precursors in raw and/or distribution system. However, there was no difference between collecting samples at the EPTDS or DSMRT and the systems were not required to sample raw water for nitrosamines.

The water systems with NDEA detections that used disinfectant with chlorine and chloramines had concentrations up to 50 ng/L and 100 ng/L, respectively. The water systems with NPYR concentrations that used disinfectant such as chlorine and chloramines had concentrations up to 24 ng/L and 17 ng/L, respectively. The water systems with NDBA and NMEA detections that used disinfectant with chlorine had concentrations up to 21 ng/L and 5 ng/L, respectively.

Chapter 5

CONCLUSIONS

Pure drinking water is not available to everyone; there are many factors that determine the condition of source water and water treatment being used for drinking water. The six nitrosamine contaminants reviewed from the CCL3 were determined to be a probable carcinogenic chemical compound. Nitrosamines were detected in 48 states based on the data analyzed from the UCMR 2 was submitted by public water systems; however detections were predominant in the state of California and Texas. However, they had more samples analyses completed than other states. There were no seasonal trends based on occurrence in the UCMR 2.

The criteria set by USEPA to determine if a contaminant should be regulated:

1. Projected adverse health effects from the contaminant
2. The extent of occurrence of the contaminant in drinking water and
3. Regulation of the contaminant presents a meaningful opportunity for reducing risks to health.

Several animal laboratories studies have shown nitrosamines have caused various health risks (Table 6). In table 6, tumors were seen to affect the liver in every experiment. Based on the adverse health effects that affected the animals, the potential adverse health effects on humans are projected to be significant with classification of a B2 carcinogen.

Table 6

Carcinogen effects of nitrosamines in animals

Nitrosamine Compounds	**Tumors**	**Animals**	**Exposure routes**
NDEA	Liver, esophageal, lung, tracheal, bronchial, forestomach & nasal cavity	Mice, hamsters, guinea pigs, rabbits, dongs, monkey	Oral
NDMA	Liver, lung, kidney, nasal cavity & bile duct	Rats, mice, hamsters, rabbits, guinea pigs	Oral
NDBA	Liver, esophageal & bladder	Rats & mice	Oral
NDPA	Liver, nasal cavity, esophagus, tongue, forestomach & lung	Rates & mice	Oral
NMEA	Liver, esophageal, renal, lung & nasal	Rats & hamsters	Oral
NPYR	Liver, testes, laryngeal, tracheal & nasal	Rats, mice & hamsters	Oral & i.p.

Source USEPA 2011

The UCMR 2 data provides results where NDMA as well as other nitrosamines detections occurs in drinking water.   Based on the UCMR 2 data, NDMA has been detected at the health level concern with concentrations up to 630 ng/L and occurrence in 45 states and/or territory. NDMA was detected at or above the MRL in 324 public water systems. There were 212 detections at or above the current California notification action level of 10 ng/L. The national occurrence is likely to be present in the nation's small and large systems. NDMA occurred in both ground water and surface water systems, but was more prevalent in surface water. Although, the other nitrosamines detections were very low, the occurrence of NDEA is relatively high.

The meaningful opportunity for reducing health risks would be based on the population that could be impacted with adverse health effects based on the animal studies and occurrence of nitrosamine detections. These findings suggest that approximately 94 million people were served by drinking water systems with detectable levels of NDMA between 2008 and 2010.

In general, to minimize disinfection byproducts, water systems must determine the suitability of water treatment based on their water type and source water. The use of various disinfectants such as chlorine and chloramines is based on the amount of organic matter in the source water, and distance from the treatment plant. Several research studies have determined the use of chloramines have formed nitrosamine disinfection byproducts.

Nitrosamines should be regulated based on the adverse health effects, and occurrence. However, in order to regulate, analytical method would need to be improved because their MRL is less than the HRL. Regulations would be needed to protect public health without causing drastic financial burden for water systems to comply with. Basically, regulations would need to take into consideration costs to systems under SDWA. The maximum contaminant level goal should be set at zero because the nitrosamines are carcinogens. All public water systems would need to sample to determine if nitrosamines are detected in the drinking water.

Recommendations

The author suggests the following recommendations for further study:

a) Research on the appropriate disinfectant based on source water due to the effects of precursors.

b) Research on individual water systems with high detection to determine specific cause of the nitrosamine formation (e.g. determining if there are any industries such as waste water facilities that could influence formation). This would enable water systems to determine the need for source water protection to avoid contamination.

c) Research on improving analytical methods for lower detection limits. Improving analytical methods would provide accurate concentrations and/or detection.

d) Research on treatment techniques may be needed if other options are not preventable.

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APPENDIX A

SUMMARY OF UCMR 2 DATA

Table A-1

Number of UCMR 2 Analytical Samples and Systems by System Type

System Size by Population Served	System Type	Systems	
		Number	Percent
Less than 10,001	CWS	466	87.8%
	NTNCWS	60	11.3%
	TNCWS	5	0.9%
	Total	531	100.0%
10,001-100,000	CWS	317	99.7%
	NTNCWS	1	0.3%
	TNCWS	0	0.0%
	Total	318	100.0%
>100,000	CWS	329	100.0%
	NTNCWS	0	0.0%
	TNCWS	0	0.0%
	Total	329	100.0%

Note: Community water system (CWS), Non-transit community water system (NTNCWS) and Transit non-community water systems (TNCWSs)

Table A-2

Summary of UCMR 2: Number of PWSs by State, System Size, by Source Water Type (Very Small, Small and Medium)

States	Very Small			Small				Medium			
	GU	GW	SW	GU	GW	MX	SW	GU	GW	MX	SW
Alaska		1	5				1				1
Alabama					2				4		
Arkansas					1		1		2		2
Arizona		1	1		1		1		2		
California		7	15		3		6		6	1	3
Colorado	1	1	3		1		3		1		2
Connecticut		2			1						1
D.C.											
Delaware									1		
Florida		4			3				4		1
Georgia		3	1		2		2	1	1		1
Guam											
Iowa									1		
Idaho		1			2		1		2		1
Illinois		1	2		1		1		1		
Indiana		1	1		3		2		3		2
Kansas		1			2		1	1	2		
Kentucky		1	1		1		2		1		2
Louisiana	1						1				2
Massachusetts		1			3		1		4		1
Maryland		1			1		1		2		1
Maine		1	1		1		1		1		1
Michigan		1			1		1				1
Minnesota		4			3		1		2		1
Missouri		2			2				2		1
Mississippi		2	1		2		1		2		2
N.Mariana Is.		1			4				5		
Mississippi		1	2		1		1				1
Montana		3	1		2		1		2		3
North Carolina			1		1		1				
North Dakota		1			1		1		1		
Nebraska		2			1		1				
New Hampshire		2			2				2		
New Jersey		1	1		1		1		1		

New Mexico		1							1		
Nevada		1	1						1		
New York	2	4	3	1	3		4		2		3
Ohio		2	1		3		2	1	2		1
Oklahoma		1	2		1		3		1		4
Oregon		1	2		1		2		1		2
Pennsylvania		4	4		4		5		2		5
Puerto Rico			5		1		3		1		2
Rhode Island		1									
South Carolina		1	1		1		1		1		1
South Dakota		1	4		1		1				
Tennessee			1				2	2	1		2
Texas		5	6		10	2	7		14		6
Utah	1				1		1		1		1
Virginia	1	2	1		2		2				3
Virgin Islands		1									
Vermont		1	1				1				1
Washington		4	2		2		1		2		1
Wisconsin		3			2				3		
West Virginia	1	1		1			2				3
Wyoming			1				1				1
Region 6					2						
Region 9			1				1				
Grand Total	7	81	72	2	83	2	73	5	88	1	66
All GW		81			83				88		
All SW		79			77				72		
TOTAL		160			160				160		

Table A-3

Summary of UCMR 2: Number of PWSs by State, System Size, by Source Water Type (Large, Very Large and X-Large)

States	Large				Very Large			X-Large			
	GU	GW	MX	SW	GW	MX	SW	GU	GW	MX	SW
Alaska											1
Alabama		4		1	1		2				6
Arkansas		1		2	1						3
Arizona		2			1				4	1	5
California		9	1	3	17	3	8		28	9	35
Colorado		1		2			1				10
Connecticut		1		1			1				5
D.C.											1
Delaware		1							1		2
Florida		9		1	22				24	4	7
Georgia		2	1	1		1	2		2		11
Guam									1		
Iowa					1				2		
Idaho		1		1	2		1	1			2
Illinois		1			1						1
Indiana		4		4			4		3		8
Kansas		3		1	2	1			1		6
Kentucky		1		1				2			4
Louisiana				5			3		1		4
Massachusetts		2		1	1		1		3		4
Maryland		4	2		1		2		1		8
Maine		2			1				1		3
Michigan				1							1
Minnesota		1		1	1	1	1		2	1	4
Missouri		3			4		2				2
Mississippi		2		1	1		1		1		4
N.Mariana Is.		3									2
Mississippi											1
Montana		2		3	1		4		1		12
North Carolina							1				
North Dakota		1						1		1	
Nebraska				1							1
New Hampshire		5		1	1		1	1	4		7
New Jersey		1			1				1		
New Mexico		1									
Nevada							1				4

New York		4		2	3		3		5		14
Ohio		4		3	3		3		2		9
Oklahoma		1		2			1				3
Oregon	1	1					1				5
Pennsylvania		1	1	2	1		4			3	15
Puerto Rico		1		3	1		2				8
Rhode Island							1				2
South Carolina				2	1		2				5
South Dakota		1								1	
Tennessee		1		4	1		4		1		4
Texas		4	3	5	2	1	6		3	8	14
Utah		2			1		1		2	1	4
Virginia				3			2				11
Virgin Islands											
Vermont							1				
Washington	1	2			8				3		3
Wisconsin		1		1	2		1		1		3
West Virginia				1			1				2
Wyoming							1				
Region 6											
Region 9											
Grand Total	2	90	8	60	83	7	70	5	98	29	266
All GW		90				83			98		
All SW		70				77			300		
TOTAL		160				160			398		

Table A-4

Number of PWS and Samples taken by State (UCMR 2)

State	Total Number of Samples	Total Number of PWSs
Alaska	582	9
Alabama	1620	20
Arkansas	696	13
Arizona	4518	19
California	26350	154
Colorado	1914	26
Connecticut	990	12
D.C.	48	1
Delaware	702	5
Florida	4758	79
Georgia	1890	31
Guam	1398	1
Hawaii	966	4
Iowa	780	15
Idaho	654	9
Illinois	2352	35
Indiana	1218	21
Kansas	840	16
Kentucky	936	17
Louisiana	1812	22
Massachusetts	1325	24
Maryland	720	13
Maine	234	6
Michigan	1530	23
Minnesota	618	18
Missouri	1002	20
N.Mariana Is.	684	15
Mississippi	288	7
Montana	2130	35
North Carolina	168	4
North Dakota	426	7
Nebraska	186	6

New Hampshire	2250	26
New Jersey	792	8
New Mexico	180	3
Nevada	882	8
New York	9240	53
Ohio	1782	36
Oklahoma	948	19
Oregon	882	17
Pennsylvania	3936	51
Puerto Rico	3414	27
Rhode Island	180	4
South Carolina	840	16
South Dakota	372	9
Tennessee	1356	23
Texas	9775	96
Utah	1200	16
Virginia	1710	27
Virgin Islands	24	1
Vermont	216	5
Washington	2100	29
Wisconsin	1284	17
West Virginia	516	12
Wyoming	198	4
Region 6	48	2
Region 9	144	2
Total	108604	1198

Table A-5

Number of UCMR 2 Analytical Samples and Systems by Source Water Type

System Size	Source Type	Samples		Systems	
		Number	Percent	Number	Percent
Very Small	GU	312	5.8%	7	4.2%
	GW	1722	31.8%	82	49.4%
	MX	72	1.3%	3	1.8%
	SW	3306	61.1%	74	44.6%
	Total	5412	100.0%	166	100.0%
Small	GU	120	1.9%	2	1.2%
	GW	2328	37.1%	86	50.6%
	MX	156	2.5%	4	2.4%
	SW	3672	58.5%	78	45.9%
	Total	6276	100.0%	170	100.0%
Medium	GU	228	3.0%	5	2.8%
	GW	3728	48.4%	89	50.0%
	MX	390	5.1%	10	5.6%
	SW	3354	43.6%	74	41.6%
	Total	7700	100.0%	178	100.0%
Large	GU	102	1.0%	3	1.6%
	GW	5994	59.1%	98	51.9%
	MX	672	6.6%	16	8.5%
	SW	3366	33.2%	72	38.1%
	Total	10134	100.0%	189	100.0%
Extra Large	GU	360	0.6%	8	1.4%
	GW	32222	49.5%	175	30.3%
	MX	8298	12.8%	82	14.2%
	SW	24200	37.2%	312	54.1%
	Total	65080	100.0%	577	100.0%
Very Large	GU	72	0.5%	2	1.0%
	GW	8328	59.5%	98	50.8%
	MX	924	6.6%	17	8.8%
	SW	4668	33.4%	76	39.4%
	Total	13992	100.0%	193	100.0%

Table A-6

Summary of UCMR 2 Occurrence of the Six Nitrosamines CCL 3 Contaminants Monitored Under UCMR 2 (by System Size)

Contaminant	System Size	Sample Level			System Level		
		No. of Samples	Detections		No. of Systems Sampled	≥ 1 Detection(s)	
			Number	Percent		Number	Percent
NDEA	Very Small	902	-	-	160	-	-
	Small	1046	-	-	160	-	-
	Medium	1285	1	0%	160	1	1%
	Large	1689	1	0%	160	1	1%
	Very Large	2322	8	0%	160	3	2%
	Extra Large	10852	36	0%	398	21	5%
	All	18096	46	0%	1198	26	2%
NDMA	Very Small	902	58	6%	160	20	13%
	Small	1046	107	10%	160	26	16%
	Medium	1285	175	14%	160	38	24%
	Large	1689	128	8%	160	32	20%
	Very Large	2334	225	10%	160	39	10%
	Extra Large	10842	1168	11%	398	169	42%
	All	18098	1861	10%	1198	324	27%
NDBA	Very Small	902	-	-	160	-	-
	Small	1046	-	-	160	-	-
	Medium	1285	3	0%	160	2	1%
	Large	1689	-	-	160	-	-
	Very Large	2334	-	-	160	-	-
	Extra Large	10845	6	0%	398	3	1%
	All	18101	9	0%	1198	5	0%

Table A-6 (Continued)

Contaminant	System Size	Sample Level			System Level		
		No. of Samples	Detections		No. of Systems Sampled	≥ 1 Detection(s)	
			Number	Percent		Number	Percent
NDPA	Very Small	902	-	-	160	-	-
	Small	1046	-	-	160	-	-
	Medium	1285	-	-	160	-	-
	Large	1689	-	-	160	-	-
	Very Large	2334	-	-	160	-	-
	Extra Large	10851	-	-	398	-	-
	All	18107	0	-	1198	-	-
NMEA	Very Small	902	1	0%	160	1	1%
	Small	1046	1	0%	160	1	1%
	Medium	1285	1	0%	160	1	1%
	Large	1689	-	-	160	-	-
	Very Large	2334	-	-	160	-	-
	Extra Large	10845	-	-	398	-	-
	All	18101	3	0%	1198	3	0%
NPYR	Very Small	902	-	-	160	-	-
	Small	1046	3	0%	160	1	1%
	Medium	1285	8	1%	160	2	1%
	Large	1689	6	0%	160	5	3%
	Very Large	2334	1	0%	160	1	1%
	Extra Large	10845	23	0%	398	12	3%
	All	18101	41	0%	1198	21	2%

Table A-7
Summary of UCMR 2 Occurrence of the Six Nitrosamines CCL 3 Contaminants Monitored Under UCMR 2 (by System Size) Analytical Detections

Contaminant	System Size	Concentration of Analytical Detections			
		Minimum	Maximum	Average	Median
NDEA	Very Small	-	-	-	-
	Small	-	-	-	-
	Medium	0.009	0.009	0.009	0.009
	Large	0.037	0.037	0.037	0.037
	Very Large	0.0051	0.05	0.0131	0.0063
	Extra Large	0.005	0.1	0.0153	0.00705
	All	0.005	0.1	0.0153	0.00705
NDMA	Very Small	0.0021	0.0846	0.0105	0.004
	Small	0.002	0.63	0.0277	0.00822
	Medium	0.002	0.13	0.0125	0.007
	Large	0.002	0.0592	0.0076	0.0064
	Very Large	0.002	0.0656	0.0072	0.00695
	Extra Large	0.002	0.094	0.0069	0.00885
	All	0.002	0.63	0.0088	0.0074
NDBA	Very Small	-	-	-	-
	Small	-	-	-	-
	Medium	0.004	0.0206	0.0103	0.00629
	Large	-	-	-	-
	Very Large	-	-	-	-
	Extra Large	0.0044	0.01	0.0074	0.00793
	All	0.004	0.0206	0.0084	0.00666

Table A-7 (Continued)

Contaminant	System Size	Concentration of Analytical Detections			
		Minimum	Maximum	Average	Median
NDPA	Very Small	-	-	-	-
	Small	-	-	-	-
	Medium	-	-	-	-
	Large	-	-	-	-
	Very Large	-	-	-	-
	Extra Large	-	-	-	-
	All	-	-	-	-
NMEA	Very Small	0.0049	0.0049	0.0049	0.0049
	Small	0.0036	0.0036	0.0036	0.0036
	Medium	0.0045	0.0045	0.0045	0.0045
	Large	-	-	-	-
	Very Large	-	-	-	-
	Extra Large	-	-	-	-
	All	0.0036	0.0049	0.0043	0.0045
NPYR	Very Small	-	-	-	-
	Small	0.0021	0.0061	0.0037	0.0028
	Medium	0.0021	0.005	0.0033	0.00292
	Large	0.0022	0.0097	0.0048	0.0054
	Very Large	0.0066	0.0066	0.0066	0.0066
	Extra Large	0.0021	0.0238	0.0061	0.00465
	All	0.0021	0.0238	0.0052	0.0041

Table A-8

Summary of UCMR 2 Occurrence of the Six Nitrosamines CCL 3 Contaminants Monitored Under UCMR 2 (by Source Water Type)

Contaminant	Source Water Type	Sample Level			System Level		
		No. of Samples	Detections		No. of Systems	Detection(s)	
			Number	Percent		Number	Percent
NDEA	GU	199	-	-	27	0	-
	GW	9048	25	0%	625	14	2.24%
	MX	1752	2	0%	132	2	1.52%
	SW	7097	19	0%	685	12	1.75%
	ALL	18096	46	0%	1469	28	1.91%
NDMA	GU	199	21	11%	27	5	18.52%
	GW	9056	197	2%	625	73	11.68%
	MX	1752	440	25%	132	66	50.00%
	SW	7091	1203	17%	685	241	35.18%
	ALL	18098	1861	10%	1469	385	26.21%
NDBA	GU	199	-	-	27	-	-
	GW	9056	9	0%	625	5	0.80%
	MX	1752	-	-	132	-	-
	SW	7094	-	-	685	-	-
	ALL	18101	9	0%	1469	5	0.34%
NDPA	GU	199	-	-	27	-	-
	GW	9060	-	-	625	-	-
	MX	1752	-	-	132	-	-
	SW	7096	-	-	685	-	-
	ALL	18107	0	0%	1469	0	0.00%

Table A-8 (Continued)

Contaminant	Source Water Type	Sample Level			System Level		
		No. of Samples	Detections		No. of Systems	Detection(s)	
			Number	Percent		Number	Percent
NMEA	GU	199	-	-	27	-	-
	GW	9056	-	-	625	-	-
	MX	1752	-	-	132	-	-
	SW	7094	3	0%	685		0.00%
	ALL	18101	3	0%	1469	0	0.00%
NPYR	GU	199	-	-	27	-	-
	GW	9056	1	0%	625	1	0.16%
	MX	1752	2	0%	132	2	1.52%
	SW	7094	38	1%	685	18	2.63%
	ALL	18101	41	0%	1469	21	1.43%

Table A-9

Summary of UCMR 2 Occurrence of the Six Nitrosamines CCL 3 Contaminants Monitored Under UCMR 2 (by Source Water Type) Analytical Detections

Contaminant	Source Water Type	Concentration of Analytical Detections			
		Minimum	Maximum	Average	Median
NDEA	GU	-	-	-	-
	GW	0.0051	0.028	0.0086	0.00665
	MX	0.0061	0.034	0.0201	0.02005
	SW	0.005	0.1	0.0236	0.0108
	ALL	0.005	0.1	0.0153	0.00705
NDMA	GU	0.0022	0.011	0.0045	0.004
	GW	0.002	0.058	0.005	0.00385
	MX	0.002	0.63	0.0106	0.0098
	SW	0.002	0.47	0.0088	0.00906
	ALL	0.002	0.63	0.0088	0.0081
NDBA	GU	-	-	-	-
	GW	0.004	0.0206	0.0084	0.00666
	MX	-	-	-	-
	SW	-	-	-	-
	ALL	0.004	0.0206	0.0084	0.00666
NDPA	GU	-	-	-	-
	GW	-	-	-	-
	MX	-	-	-	-
	SW	-	-	-	-
	ALL	-	-	-	-

Table A-9 (Continued)

Contaminant	Source Water Type	Concentration of Analytical Detections			
		Minimum	Maximum	Average	Median
NMEA	GU	-	-	-	-
	GW	-	-	-	-
	MX	-	-	-	-
	SW	0.0036	0.0049	0.0043	0.0045
	ALL	0.0036	0.0049	0.0043	0.0045
NPYR	GU	-	-	-	-
	GW	0.0036	0.0036	0.0036	0.0036
	MX	0.0055	0.006	0.0058	0.00575
	SW	0.0021	0.0238	0.0052	0.0043
	ALL	0.0021	0.0238	0.0052	0.0045

Table A-10

NDEA Occurrence Based on Samples and Systems

Water Type	System Size by Population Served	Sample Level			System Level		
		Total Number of Samples	Detections		Total Number of Systems Sampled	Systems with Detections	
			Number	Percent		Number	Percent
Ground Water	<500	326	0	0.0%	90	0	0%
	501-3300	402	0	0.0%	80	0	0%
	3301-10000	642	1	0.2%	80	1	1%
	10001-100000	2106	4	0.2%	134	3	2%
	100001-1000000	4355	20	0.5%	62	10	16%
	>100000	1204	0	0.0%	2	0	0%
	Total	9035	25	0.3%	448	14	3%
Surface Water	<500	920	0	0.0%	105	0	0%
	501-3300	718	1	0.1%	84	1	1%
	3301-10000	725	0	0.0%	92	0	0%
	10001-100000	1642	2	0.1%	183	1	1%
	100001-1000000	4316	10	0.2%	267	6	2%
	>100000	607	8	1.3%	18	0	0%
	Total	8928	21	0.2%	749	8	1%

Table A-11

NDEA Occurrence Based on Population Served

Water Type	System Size by Population Served	Population Served-Level		
		Total Population Served	Pop, Served by Systems with Detections	
			Number	Percent
Ground Water	<500	13519	0	0%
	501-3300	98601	0	0%
	3301-10000	461611	7022	2%
	10001-100000	5951126	194888	3%
	100001-1000000	12321941	1567846	13%
	>100000	3200000	0	0%
	Total	22046798	1769756	8%
Surface Water	<500	17537	0	0%
	501-3300	146305	3153	2%
	3301-10000	581032	0	0%
	10001-100000	9074947	68656	1%
	100001-1000000	68702355	962512	1%
	>100000	37145091	0	0%
	Total	115667267	1034321	1%

Table A-12

NDEA System Level Occurrence by State & Size Category (PWS)

State	Total Number of Samples	Total Number of PWSs						
		VS	S	M	L	VL	XL	Total
Arizona	4518	2	2	2	2	1	10	19
California	26350	22	9	10	13	28	72	154
Florida	4758	4	3	5	10	22	35	79
Guam	1398						1	1
Maryland	720	2	2	2	2	1	4	13
Maine	234	1	2	1	1		1	6
Minnesota	618	2	2	3	3	6	2	18
Pennsylvania	3936	8	9	7	4	5	18	51
South Carolina	840	2	2	2	2	3	5	16
Total	43372	43	31	32	37	66	148	357

Table A-13

NDEA System Level Occurrence by State & Size Category (Detections)

State	Number of PWSs with Detections							Percentage of PWSs with Detections
	VS	S	M	L	VL	XL	Total	
Arizona						2	2	11%
California			1		2	11	14	9%
Florida						3	3	4%
Guam						1	1	100%
Maryland						1	1	8%
Maine						1	1	17%
Minnesota					1		1	6%
Pennsylvania					1	1	2	4%
South Carolina				1			1	6%
Total	0		1	1	4	20	26	7%

Table A-14

NDEA System Level Occurrence by State & Source Water Type

State	Total Number of PWSs			Number of PWSs with Detections		
	GW	SW	Total	GW	SW	Total
Arizona	1	8	9	1	1	2
California	70	84	154	8	7	15
Florida	15	17	32	3	0	3
Guam	1	0	1	1	0	1
Maryland	7	6	13	0	1	1
Maine	2	4	6	0	1	1
Minnesota	13	5	18	0	1	1
Pennsylvania	12	39	51	1	2	3
South Carolina	4	12	16	0	1	1
Total	125	175	300	14	14	28

Table A-15

NDEA System Level Occurrence by State & Source Water Type (Percentages)

State	Percentage of PWSs with Detections		
	GW	SW	Total
Arizona	100%	13%	22%
California	11%	8%	10%
Florida	20%	0%	9%
Guam	100%	0%	100%
Maryland	0%	17%	8%
Maine	0%	25%	17%
Minnesota	0%	20%	6%
Pennsylvania	8%	5%	6%
South Carolina	0%	8%	6%
Total	11%	8%	9%

Table A-16

NDEA Statistics for All Detections by State (Min, Median, 99th Percentile, Max)

State	Total Number of Detections	Statistics for Detections (in ug/L)			
		Minimum	Median	99th Percentile	Maximum
Arizona	3	0.0061	0.0068	0.036396	0.01
California	22	0.005	0.00645	0.07429	0.085
Florida	5	0.006	0.0062	0.021372	0.022
Guam	1	0.0058	0.0058	0.0058	0.0058
Maine	2	0.0066	0.0533	0.099066	0.1
Maryland	6	0.007	0.016	0.0258	0.026
Minnesota	1	0.0068	0.0068	0.0068	0.0068
Pennsylvania	5	0.0086	0.012	0.04852	0.05
South Carolina	1	0.037	0.037	0.037	0.037
Total	46	0.005	0.00705	0.09325	0.1

Table A-17

NDMA Occurrence Based on Samples and Systems

Water Type	System Size by Population Served	Sample Level			System Level		
		Total Number of Samples	Detections		Total Number of Systems Sampled	Systems with Detections	
			Number	Percent		Number	Percent
Ground Water	<500	326	2	1%	88	2	2%
	501-3300	402	9	2%	84	6	7%
	3301-10000	642	12	2%	93	8	9%
	10001-100000	2118	57	3%	188	17	9%
	100001-1000000	4353	92	2%	166	37	22%
	>100000	1202	25	2%	8	3	38%
	Total	9043	197	2%	627	73	12%
Surface Water	<500	943	109	12%	111	26	23%
	501-3300	726	94	13%	85	22	26%
	3301-10000	725	189	26%	90	36	40%
	10001-100000	1682	235	14%	168	48	29%
	100001-1000000	4354	885	20%	260	112	43%
	>100000	607	152	25%	17	7	41%
	Total	9037	1664	18%	731	251	34%

Table A-18

NDMA Occurrence Based on Population Served

Water Type	System Size by Population Served	Population Served-Level		
		Total Population Served	Pop, Served by Systems with Detections	
			Number	Percent
Ground Water	<500	13519	799	6%
	501-3300	98601	6216	6%
	3301-10000	461611	47895	10%
	10001-100000	5951126	840488	14%
	100001-1000000	12321941	7413295	60%
	>100000	3200000	5299000	166%
	Total	22046798	13607693	62%
Surface Water	<500	17537	3536	20%
	501-3300	146305	38374	26%
	3301-10000	581032	235013	40%
	10001-100000	9074947	2693311	30%
	100001-1000000	68702355	30893156	45%
	>100000	37145091	12083814	33%
	Total	115667267	45947204	40%

Table A-19

NDMA System Level Occurrence by State & Size Category

State	Total Number of Samples	Total Number of PWSs							Number of PWSs with Detections						
		VS	S	M	L	VL	XL	Total	VS	S	M	L	VL	XL	Total
Alaska	582	6	1	1			1	9	2						2
Alabama	1620		2	4	5	3	6	20				1		1	2
Arkansas	696		2	4	3	1	3	13			1				1
Arizona	4518	2	2	2	2	1	10	19		1				3	4
California	26350	22	9	10	13	28	72	154	5	1	2	3	11	47	69
Colorado	1914	5	4	3	3	1	10	26						6	6
Connecticut	990	2	1	1	2	1	5	12			1	1		1	3
Delaware	702			1	1		3	5						1	1
Florida	4758	4	3	5	10	22	35	79				3	4	13	20
Georgia	1890	4	4	3	4	3	13	31		1		1	1		3
Guam	1398						1	1						1	1
Iowa	780	1	3	3	2	3	3	15		1	1	1		2	5
Idaho	654	3	2	1	1	1	1	9	1						1
Illinois	2352	2	5	5	8	4	11	35	1	1	2	3	2	4	13
Indiana	1218	1	3	3	4	3	7	21						6	6
Kansas	840	2	3	3	2		6	16	1	1	2	1		5	10
Kentucky	936	1	1	2	5	3	5	17					1	2	3
Louisiana	1812	1	4	5	3	2	7	22		1		1	1	4	7

Massachusetts	1325	1	2	3	6	3	9	24					1	4	5
Maryland	720	2	2	2	2	1	4	13						1	1
Maine	234	1	2	1	1		1	6			1	1			2
Michigan	1530	4	4	3	2	3	7	23		1	1		1	2	5
Minnesota	618	2	2	3	3	6	2	18			2		1	2	5
Missouri	1002	3	3	4	3	2	5	20			1	1	1	4	7
Mississippi	288	1	4	5	3		2	15						2	2
Montana	2130	3	2	1			1	7	1	1					2
North Carolina	168	4	3	5	5	5	13	35		1	1	1	2	3	8
North Dakota	426	1	2			1		4	1	1			1		3
Nebraska	186	1	2	1	1		2	7						2	2
New Hampshire	2250	2	2		1		1	6						1	1
New Jersey	792	2	2	2	6	2	12	26						1	1
New York	9240	2	2	1	1	1	1	8	2		2			1	5
Ohio	1782	3	5	4	7	6	11	36	1	1	1			2	5
Oklahoma	948	3	4	5	3	1	3	19	1	1	1			2	5
Oregon	882	3	3	3	2	1	5	17		1					1
Pennsylvania	3936	8	9	7	4	5	18	51			3	2	1	10	16
Puerto Rico	3414	5	4	3	4	3	8	27						1	1
South Carolina	840	2	2	2	2	3	5	16			1	2	1	4	8
South Dakota	372	5	2		1		1	9	1						1
Tennessee	1356	1	2	5	5	5	5	23			1		1		2
Texas	9775	11	19	20	12	9	25	96	2	10	10	8	6	21	57
Utah	1200	1	2	2	2	2	7	16						2	2
Virginia	1710	4	4	3	3	2	11	27				1	1	6	8
Vermont	216	2	1	1		1		5					1		1

Washington	2100	6	3	3	3	8	6	29		2	2		1	2	7
Wisconsin	1284	3	2	3	2	3	4	17	1						1
West Virginia	516	2	3	3	1	1	2	12			1	1			2
Total	105250	144	148	151	153	150	370	1116	20	26	37	32	39	169	323

Table A-20

NDMA System Level Occurrence by State & Size Category (Detections)

State	Total Number of Samples	Number of PWSs with Detections							% of PWSs with Detections
		VS	S	M	L	VL	XL	Total	
Alaska	582	2						2	22%
Alabama	1620				1		1	2	10%
Arkansas	696			1				1	8%
Arizona	4518		1				3	4	21%
California	26350	5	1	2	3	11	47	69	45%
Colorado	1914						6	6	23%
Connecticut	990			1	1		1	3	25%
Delaware	702						1	1	20%
Florida	4758				3	4	13	20	25%
Georgia	1890		1		1	1		3	10%
Guam	1398						1	1	100%
Iowa	780		1	1	1		2	5	33%
Idaho	654	1						1	11%
Illinois	2352	1	1	2	3	2	4	13	37%
Indiana	1218						6	6	29%
Kansas	840	1	1	2	1		5	10	63%
Kentucky	936					1	2	3	18%
Louisiana	1812		1		1	1	4	7	32%
Massachusetts	1325					1	4	5	21%
Maryland	720						1	1	8%
Maine	234			1	1			2	33%
Michigan	1530		1	1		1	2	5	22%
Minnesota	618			2		1	2	5	28%
Missouri	1002			1	1	1	4	7	35%
Mississippi	288						2	2	13%
Montana	2130	1	1					2	29%
North Carolina	168		1	1	1	2	3	8	23%
North Dakota	426	1	1			1		3	75%
Nebraska	186						2	2	29%
New Hampshire	2250						1	1	17%
New Jersey	792						1	1	4%
New York	9240	2		2			1	5	63%
Ohio	1782	1	1	1			2	5	14%
Oklahoma	948	1	1	1			2	5	26%

Oregon	882		1					1	6%
Pennsylvania	3936			3	2	1	10	16	31%
Puerto Rico	3414						1	1	4%
South Carolina	840			1	2	1	4	8	50%
South Dakota	372	1						1	11%
Tennessee	1356			1		1		2	9%
Texas	9775	2	10	10	8	6	21	57	59%
Utah	1200						2	2	13%
Virginia	1710				1	1	6	8	30%
Vermont	216					1		1	20%
Washington	2100		2	2		1	2	7	24%
Wisconsin	1284	1						1	6%
West Virginia	516			1	1			2	17%
Total	105250	20	26	37	32	39	169	323	29%

Table A-21

NDMA System Level Occurrence by State & Source Water Type

State	Total Number of PWSs			Number of PWSs with Detections			Percentage of PWSs with Detections		
	GW	SW	Total	GW	SW	Total	GW	SW	Total
Alaska	2	8	10		2	2	0%	25%	20%
Alabama	13	11	24		3	3	0%	27%	13%
Arkansas	5	8	13		1	1	0%	13%	8%
Arizona	17	12	29	1	3	4	6%	25%	14%
California	108	111	219	29	55	84	27%	50%	38%
Colorado	6	22	28		6	6	0%	27%	21%
Connecticut	7	8	15	2	2	4	29%	25%	27%
Delaware	3	3	6		1	1	0%	33%	17%
Florida	70	14	84	12	8	20	17%	57%	24%
Georgia	12	22	34	1	2	3	8%	9%	9%
Guam	1		1	1		1	100%	0%	100%
Iowa	8	7	15		5	5	0%	71%	33%
Idaho	6	4	10		1	1	0%	25%	10%
Illinois	16	21	37	1	13	14	6%	62%	38%
Indiana	12	10	22	1	5	6	8%	50%	27%
Kansas	4	12	16		10	10	0%	83%	63%
Kentucky	1	16	17		3	3	0%	19%	18%
Louisiana	14	8	22		7	7	0%	88%	32%
Massachusetts	11	15	26		5	5	0%	33%	19%
Maryland	8	7	15		1	1	0%	14%	7%
Maine	2	4	6		2	2	0%	50%	33%
Michigan	13	10	23	2	4	6	15%	40%	26%
Minnesota	13	5	18	1	4	5	8%	80%	28%
Missouri	11	10	21	1	6	7	9%	60%	33%
Mississippi	13	2	15		2	2	0%	100%	13%
Montana	2	5	7		3	3	0%	60%	43%
North Carolina	11	24	35	2	6	8	18%	25%	23%
North Dakota	1	3	4	1	2	3	100%	67%	75%
Nebraska	6	3	9		2	2	0%	67%	22%
New Hampshire	3	3	6		1	1	0%	33%	17%
New Jersey	18	15	33		1	1	0%	7%	3%
New York	22	34	56	3	2	5	14%	6%	9%
Ohio	19	20	39		5	5	0%	25%	13%
Oklahoma	4	15	19		5	5	0%	33%	26%
Oregon	7	14	21		1	1	0%	7%	5%
Pennsylvania	17	39	56	2	15	17	12%	38%	30%

Puerto Rico	4	23	27		1	1	0%	4%	4%
South Carolina	4	12	16		8	8	0%	67%	50%
South Dakota	3	7	10		1	1	0%	14%	10%
Tennessee	4	19	23		2	2	0%	11%	9%
Texas	51	66	117	7	57	64	14%	86%	55%
Utah	11	9	20		2	2	0%	22%	10%
Virginia	6	23	29		8	8	0%	35%	28%
Vermont	1	4	5		1	1	0%	25%	20%
Washington	22	10	32	5	2	7	23%	20%	22%
Wisconsin	12	5	17	1		1	8%	0%	6%
West Virginia	1	11	12		2	2	0%	18%	17%
Total	605	714	1319	73	278	351	12%	39%	27%

Table A-22

NDMA Statistics for All Detections by State (Min, Median, 99th Percentile, Max)

State	Total Number of Detections	Statistics for Detections (in ug/L)			
		Minimum	Median	99th Percentile	Maximum
Alaska	9	0.00216	0.0025	0.010648	0.0108
Alabama	3	0.0022	0.0024	0.002596	0.0026
Arkansas	6	0.003	0.00549	0.021307	0.022
Arizona	7	0.0029	0.0068	0.03174	0.033
California	491	0.002	0.0063	0.0553	0.058
Colorado	51	0.002	0.00485	0.02125	0.023
Connecticut	9	0.0021	0.0034	0.0044744	0.0045
Delaware	7	0.0031	0.004	0.007044	0.0072
Florida	79	0.002	0.0052	0.0855	0.094
Georgia	4	0.00309	0.00452	0.0057231	0.00573
Guam	2	0.002	0.0023	0.002594	0.0026
Iowa	25	0.0027	0.00545	0.028507	0.0313
Idaho	1	0.0026	0.0026	0.0026	0.0026
Illinois	60	0.002	0.006	0.03983	0.045
Indiana	21	0.002	0.0029	0.005885	0.0059
Kansas	34	0.002	0.0039	0.009964	0.011
Kentucky	13	0.00277	0.00605	0.01467	0.015
Louisiana	35	0.002	0.00795	0.03525	0.036
Massachusetts	10	0.002	0.00315	0.0061578	0.00626
Maryland	10	0.0024	0.003	0.005424	0.0056
Maine	8	0.0031	0.01541	0.0430536	0.044
Michigan	23	0.002	0.00288	0.008632	0.0088
Minnesota	20	0.0022	0.00621	0.07146	0.082
Missouri	36	0.00207	0.00352	0.01888	0.0195
Mississippi	14	0.00237	0.00498	0.0479482	0.05183
Montana	3	0.0021	0.004	0.007724	0.0078
North Carolina	21	0.00218	0.0035	0.012133	0.013
North Dakota	12	0.0022	0.00376	0.0072256	0.00734
Nebraska	9	0.0022	0.00285	0.003851	0.0039
New Hampshire	2	0.0025	0.003	0.00349	0.0035

New Jersey	3	0.0032	0.004	0.01086	0.011
New York	21	0.00201	0.00321	0.01237	0.01343
Ohio	5	0.00235	0.00285	0.0032967	0.0033
Oklahoma	32	0.0021	0.0074	0.0781708	0.08458
Oregon	2	0.0038	0.0039	0.003998	0.004
Pennsylvania	71	0.002	0.0047	0.03088	0.034
Puerto Rico	2	0.0025	0.00435	0.006163	0.0062
South Carolina	34	0.0021	0.00355	0.009501	0.0099
South Dakota	6	0.00229	0.00288	0.003687	0.0037
Tennessee	10	0.00236	0.00415	0.008237	0.0083
Texas	583	0.002	0.01182	0.249	0.63
Utah	3	0.002	0.0022	0.0036308	0.00366
Virginia	43	0.002	0.00355	0.0068	0.0071
Vermont	4	0.0022	0.0027	0.00397	0.004
Washington	14	0.002	0.0032	0.008178	0.0082
Wisconsin	1	0.00632	0.00632	0.00632	0.00632
West Virginia	2	0.0025	0.00282	0.0031237	0.00313
Total	1861	0.002	0.0055	0.0772752	0.63

Table A-23

NDBA Occurrence Based on Samples and Systems

Water Type	System Size by Population Served	Sample Level			System Level		
		Total Number of Samples	Detections		Total Number of Systems Sampled	Systems with Detections	
			Number	Percent		Number	Percent
Ground Water	<500	326	0	0.0%	88	0	0%
	501-3300	402	0	0.0%	84	0	0%
	3301-10000	642	3	0.5%	93	2	2%
	10001-100000	2127	0	0.0%	188	0	0%
	100001-1000000	4353	3	0.1%	166	2	1%
	>100000	1202	3	0.2%	8	1	13%
	Total	9052	9	0.1%	627	5	1%
Surface Water	<500	943	0	0.0%	111	0	0%
	501-3300	726	0	0.0%	85	0	0%
	3301-10000	725	0	0.0%	90	0	0%
	10001-100000	1682	0	0.0%	168	0	0%
	100001-1000000	4354	0	0.0%	260	0	0%
	>100000	607	0	0.0%	17	0	0%
	Total	9037	0	0.0%	731	0	0%

Table A-24

NDBA Occurrence Based on Population Served

Water Type	System Size by Population Served	Population Served-Level		
		Total Population Served	Pop, Served by Systems with Detections	
			Number	Percent
Ground Water	<500	13519	0	0%
	501-3300	98601	0	0%
	3301-10000	461611	14698	3%
	10001-100000	5951126	0	0%
	100001-1000000	12321941	628711	5%
	>100000	3200000	1100000	34%
	Total	22046798	1743409	8%
Surface Water	<500	17537	0	0%
	501-3300	146305	0	0%
	3301-10000	581032	0	0%
	10001-100000	9074947	0	0%
	100001-1000000	68702355	0	0%
	>100000	37145091	0	0%
	Total	115667267	0	0%

Table A-25

NDBA System Level Occurrence by State & Size Category (PWS)

State	Total Number of Samples	Total Number of PWSs						
		VS	S	M	L	VL	XL	Total
California	26350	22	9	10	13	28	72	154
Georgia	1890	4	4	3	4	3	13	31
Nevada	882	2		1		1	4	8
New York	9240	9	8	5	6	6	19	53
Total	38362	37	21	19	23	38	108	246

Table A-26

NDBA System Level Occurrence by State & Size Category (Detections)

State	Total Samples	Number of PWSs with Detections							PWSs with Detections
		VS	S	M	L	VL	XL	Total	
California	26350						2	2	1%
Georgia	1890			1				1	3%
Nevada	882			1				1	13%
New York	9240						1	1	2%
Total	38362	0	0	2	0	0	3	5	2%

Table A-27

NDBA System Level Occurrence by State & Source Water Type

State	Total Number of PWSs			Number of PWSs with Detections			Percentage of PWSs with Detections		
	GW	SW	Total	GW	SW	Total	GW	SW	Total
California	70	84	154	2	0	2	3%	0%	1%
Georgia	10	21	31	1	0	1	10%	0%	3%
Nevada	2	6	8	1	0	1	50%	0%	13%
New York	21	32	53	1	0	1	5%	0%	2%
Total	103	143	246	5	0	5	5%	0%	2%

Table A-28

NDBA Statistics for All Detections by State (Min, Median, 99th Percentile, Max)

State	Total Number of Detections	Statistics for Detections (in ug/L)			
		Minimum	Median	99th Percentile	Maximum
California	3	0.0048	0.00998	0.0092	0.01
Georgia	1	0.004	0.004	0.004	0.004
Nevada	2	0.00629	0.02048	0.013455	0.02062
New York	3	0.00442	0.00925	0.00666	0.0093
Total	9	0.004	0.01977	0.00666	0.02062

Table A-29

NMEA Occurrence Based on Samples and Systems

Water Type	System Size by Population Served	Sample Level			System Level		
		Total Number of Samples	Detections		Total Number of Systems Sampled	Systems with Detections	
			Number	Percent		Number	Percent
Ground Water	<500	326	0	0.0%	88	0	0%
	501-3300	402	0	0.0%	84	0	0%
	3301-10000	642	0	0.0%	93	0	0%
	10001-100000	2127	0	0.0%	188	0	0%
	100001-1000000	4354	0	0.0%	166	0	0%
	>100000	1202	0	0.0%	8	0	0%
	Total	9053	0	0.0%	627	0	0%
Surface Water	<500	943	1	0.1%	111	1	1%
	501-3300	726	1	0.1%	85	1	1%
	3301-10000	725	1	0.1%	90	1	1%
	10001-100000	1682	0	0.0%	168	0	0%
	100001-1000000	4354	0	0.0%	260	0	0%
	>100000	607	0	0.0%	17	0	0%
	Total	9037	3	0.0%	731	3	0%

Table A-30

NMEA Occurrence Based on Population Served

Water Type	System Size by Population Served	Population Served-Level		
		Total Population Served	Pop, Served by Systems with Detections	
			Number	Percent
Ground Water	<500	13519	0	0%
	501-3300	98601	0	0%
	3301-10000	461611	0	0%
	10001-100000	5951126	0	0%
	100001-1000000	12321941	0	0%
	>100000	3200000	0	0%
	Total	22046798	0	0%
Surface Water	<500	17537	456	3%
	501-3300	146305	710	0%
	3301-10000	581032	4509	1%
	10001-100000	9074947	0	0%
	100001-1000000	68702355	0	0%
	>100000	37145091	0	0%
	Total	115667267	5675	0%

Table A-31

NMEA System Level Occurrence by State & Size Category (PWS)

State	Total Number of Samples	Total Number of PWSs						
		VS	S	M	L	VL	XL	Total
Oklahoma	948	3	4	5	3	1	3	19
Washington	2100	6	3	3	3	8	6	29
Total	3048	9	7	8	6	9	9	48

Table A-32

NMEA System Level Occurrence by State & Size Category (Detections)

State	Total Samples	Number of PWSs with Detections							PWSs with Detections
		VS	S	M	L	VL	XL	Total	
Oklahoma	948	1	1					2	11%
Washington	2100			1				1	3%
Total	3048	1	1	1	0	0	0	3	6%

Table A-33

NMEA System Level Occurrence by State & Source Water Type

State	Total Number of PWSs			Number of PWSs with Detections			Percentage of PWSs with Detections		
	GW	SW	Total	GW	SW	Total	GW	SW	Total
Oklahoma	4	15	19	0	2	2	0%	13.3%	11%
Washington	21	8	29	0	1	1	0%	12.5%	3%
Total	25	23	48	0	3	3	0%	13.0%	6%

Table A-34

NMEA Statistics for All Detections by State (Min, Median, 99th Percentile, Max)

State	Total Number of Detections	Statistics for Detections (in ug/L)			
		Minimum	Median	99th Percentile	Maximum
Oklahoma	2	0.0036	0.00425	0.004887	0.0049
Washington	1	0.0045	0.0045	0.0045	0.0045
Total	3	0.0036	0.0045	0.004892	0.0049

Table A-35

NPYR Occurrence Based on Samples and Systems

Water Type	System Size by Population Served	Sample Level			System Level		
		Total Number of Samples	Detections		Total Number of Systems Sampled	Systems with Detections	
			Number	Percent		Number	Percent
Ground Water	<500	326	0	0.0%	88	0	0%
	501-3300	402	0	0.0%	84	0	0%
	3301-10000	642	0	0.0%	93	0	0%
	10001-100000	2127	0	0.0%	188	0	0%
	100001-1000000	4353	1	0.0%	166	1	1%
	>100000	1202	0	0.0%	8	0	0%
	Total	9052	1	0.0%	627	1	0%
Surface Water	<500	943	0	0.0%	111	0	0%
	501-3300	726	4	0.6%	85	2	2%
	3301-10000	725	8	1.1%	90	2	2%
	10001-100000	1682	7	0.4%	168	6	4%
	100001-1000000	4354	3	0.1%	260	8	3%
	>100000	607	2	0.3%	17	2	12%
	Total	9037	24	0.3%	731	20	3%

Table A-36

NPYR Occurrence Based on Population Served

Water Type	System Size by Population Served	Population Served-Level		
		Total Population Served	Pop, Served by Systems with Detections	
			Number	Percent
Ground Water	<500	13519	0	0%
	501-3300	98601	0	0%
	3301-10000	461611	0	0%
	10001-100000	5951126	0	0%
	100001-1000000	12321941	141000	1%
	>100000	3200000	0	0%
	Total	22046798	141000	1%
Surface Water	<500	17537	0	0%
	501-3300	146305	5662	4%
	3301-10000	581032	11629	2%
	10001-100000	9074947	253226	3%
	100001-1000000	68702355	1735223	3%
	>100000	37145091	5194764	14%
	Total	115667267	7200504	6%

Table A-37

NPYR System Level Occurrence by State & Size Category (PWS)

State	Total Number of Samples	Total Number of PWSs						
		VS	S	M	L	VL	XL	Total
California	26350	22	9	10	13	28	72	154
Iowa	780	1	3	3	2	3	3	15
Illinois	2352	2	5	5	8	4	11	35
Indiana	1218	1	3	3	4	3	7	21
Missouri	1002	3	3	4	3	2	5	20
New Jersey	792	2	2	2	6	2	12	26
Oklahoma	948	3	4	5	3	1	3	19
Pennsylvania	3936	8	9	7	4	5	18	51
South Carolina	840	2	2	2	2	3	5	16
Texas	9775	11	19	20	12	9	25	96
West Virginia	516	2	3	3	1	1	2	12
Total	108604	57	62	64	58	61	163	465

Table A-38

NPYR System Level Occurrence by State & Size Category (Detections)

State	Total Number of Samples	Number of PWSs with Detections							Percentage of PWSs with Detections
		VS	S	M	L	VL	XL	Total	
California	26350						2	2	1%
Iowa	780						1	1	7%
Illinois	2352					1	1	2	6%
Indiana	1218						2	2	10%
Missouri	1002						1	1	5%
New Jersey	792						2	2	8%
Oklahoma	948				1			1	5%
Pennsylvania	3936				2			2	4%
South Carolina	840				1		1	2	13%
Texas	9775		1	2				3	3%
West Virginia	516						1	1	8%
Total	108604	0	1	2	4	1	11	19	4%

Table A-39

NPYR System Level Occurrence by State & Source Water Type

State	Total Number of PWSs			Number of PWSs with Detections			Percentage of PWSs with Detections		
	GW	SW	Total	GW	SW	Total	GW	SW	Total
California	35	154	189	0	2	2	0%	1%	1%
Iowa	9	15	24	0	1	1	0%	7%	4%
Illinois	14	35	49	1	2	3	7%	6%	6%
Indiana	10	21	31	0	2	2	0%	10%	6%
Missouri	10	20	30	0	1	1	0%	5%	3%
New Jersey	11	26	37	0	2	2	0%	8%	5%
Oklahoma	3	19	22	0	1	1	0%	5%	5%
Pennsylvania	10	51	61	0	2	2	0%	4%	3%
South Carolina	4	16	20	0	1	1	0%	6%	5%
Texas	29	96	125	0	5	5	0%	5%	4%
West Virginia	1	12	13	0	1	1	0%	8%	8%
Total	136	465	601	1	20	21	1%	4%	3%

Table A-40

NPYR Statistics for All Detections by State (Min, Median, 99th Percentile, Max)

State	Total Number of Detections	Statistics for Detections (in ug/L)			
		Minimum	Median	99th Percentile	Maximum
California	2	0.0022	0.00385	0.005467	0.0055
Iowa	3	0.003	0.00302	0.006094	0.0061
Illinois	4	0.0066	0.0068	0.023152	0.0238
Indiana	5	0.003	0.0041	0.005268	0.0053
Missouri	1	0.0057	0.0057	0.0057	0.0057
New Jersey	5	0.0021	0.0033	0.017088	0.0172
Oklahoma	1	0.0054	0.0054	0.0054	0.0054
Pennsylvania	3	0.0022	0.0035	0.00595	0.006
South Carolina	1	0.0097	0.0097	0.0097	0.0097
Texas	14	0.00207	0.00282	0.005957	0.0061
West Virginia	1	0.0048	0.0048	0.0048	0.0048
Total	40	0.00207	0.0039	0.02116	0.0238