

Six-Year Review 3 Technical Support Document for Chlorate

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Abbreviations

AMWA	Association of Metropolitan Water Agencies
AWWA	American Water Works Association
AwwaRF	American Water Works Association Research Foundation
BMD	Benchmark Dose
BMDL	Benchmark Dose Level
CAGC	Chloramine Formed from Gaseous Chlorine
CAOF	Chloramine Formed from Off-Site Hypochlorite
CAON	Chloramine Formed from On-Site Hypochlorite
CAS	Chemical Abstracts Service
CCL 3	Third Contaminant Candidate List
CCR	Consumer Confidence Report
CDR	Chemical Data Reporting
CLDO	Chlorine Dioxide
CLGA	Gaseous Chlorine
CLOF	Off-site Generated Hypochlorite Stored as Liquid
CLON	On-site Generated Hypochlorite with No Storage
CSFII	Continuing Survey of Food Intakes by Individuals
CWS	Community Water System
CWSS	Community Water System Survey
DBP	Disinfection Byproducts
DBP ICR	Disinfection Byproducts Information Collection Rule
D/DBPR	Disinfectants and Disinfection Byproducts Rule
DL	Detection Limit
EP	Entry Point to the Distribution System
EPA	U.S. Environmental Protection Agency
EWG	Environmental Working Group
G6PD	Glucose-6-Phosphate Dehydrogenase
GAC	Granular Activated Carbon
GW	Ground Water
GWUDI	Ground Water Under the Direct Influence of Surface Water
HSDB	Hazardous Substances Data Bank
HRL	Health Reference Level
2xHRL	Twice the HRL
3xHRL	Three times the HRL
IUR	Inventory Update Reporting
LC-MS/MS	Liquid Chromatography and Tandem Mass Spectrometry
LOAEL	Lowest Observed Adverse Effect Level
LRAA	Locational Running Annual Average
MAC	Maximum Acceptable Concentration
MCL	Maximum Contaminant Level
MCLG	Maximum Contaminant Level Goal
MDBP	Microbial and Disinfection Byproduct
MDL	Method Detection Limit

MDDC	Missis 1/Disinfration Due de sta Conservit
MDPC	Microbial/Disinfection Products Council
MR	Location of Maximum Residence Time within the Distribution System
MRL	Minimum Reporting Level
MSR	Method Sensitivity Ratio
NCFAP	National Center for Food and Agricultural Policy
NOAEL	No Observed Adverse Effect Level
NODU	No Disinfection
NTNCWS	Non-Transient Non-Community Water System
NTP	National Toxicology Program
OPP	Office of Pesticide Programs
OSG	On-Site Generated or On-Site Generation
OTHD	All Other Types of Disinfectant
OZON	Ozone
PAC	Powdered Activated Carbon
PWS	Public Water System
PWSID	Public Water System Identification
RBC	Red Blood Cell
RD 3	Third Round of Regulatory Determinations
RfD	Reference Dose
RSC	Relative Source Contribution
RSD	Relative Standard Deviation
SM	Standard Method
SDWIS/Fed	Safe Drinking Water Information System/Federal Version
SW	Surface Water
THMs	Trihalomethanes
TRI	Toxics Release Inventory
TSC	Technical Service Center
TSH	Thyroid Stimulating Hormone
UCMR 1	First Unregulated Contaminant Monitoring Regulation
UCMR 2	Second Unregulated Contaminant Monitoring Regulation
UCMR 3	Third Unregulated Contaminant Monitoring Regulation
UF	Uncertainty Factor
ULVL	Ultraviolet Light
USACE	US Army Corps of Engineers
USEPA	U.S. Environmental Protection Agency
USGS	United States Geological Survey
UV	Ultraviolet
WHO	World Health Organization
WRF	Water Research Foundation
VV 1X1	water research roundation

1 Introduction

The Safe Drinking Water Act requires the United States Environmental Protection Agency (EPA) to conduct a periodic review of existing National Primary Drinking Water Regulations and determine which, if any, are candidates for revision. The purpose of the review, called the Six-Year Review, is to evaluate current information for each National Primary Drinking Water Regulation to determine if there is new information on health effects, treatment technology, analytical methods, occurrence and exposure, implementation and/or other factors that provide a health or technical basis to support a regulatory revision that will improve or strengthen public health protection.

Under Six-Year Review 3, EPA is reviewing the regulated chemical, radiological and microbiological contaminants included in previous reviews, as well as the Microbial and Disinfection Byproducts (MDBP) regulations that were promulgated under the following actions: the Disinfectants and Disinfection Byproduct Rules (D/DBPRs), the Surface Water Treatment Rules, the Ground Water Rule and the Filter Backwash Recycling Rule. The Surface Water Treatment Rules consist of the Surface Water Treatment Rule, the Interim Enhanced Surface Water Treatment Rule, the Long Term 1 Enhanced Surface Water Treatment Rule (LT1) and the Long Term 2 Enhanced Surface Water Treatment Rule (LT2). This is the first time that EPA is reviewing the MDBP rules. For more information about the Six-Year Review of the D/DBPRs, the reader is referred to EPA's *Six-Year Review 3 Technical Support Document for Disinfectants/Disinfection Byproducts Rules* (USEPA, 2016a). Under the SYR3, EPA also is evaluating unregulated DBPs: for example, chlorate and nitrosamines.

Chlorate was included on EPA's Third Contaminant Candidate List (CCL 3) and evaluated as a candidate for regulation under the Regulatory Determinations 3 (RD 3) program in 2014. In the Federal Register notice for Preliminary Regulatory Determination 3 (79 FR 62715, USEPA, 2014a), the Agency stated that "because chlorate and nitrosamines are DBPs that can be introduced or formed in public water systems (PWSs) partly because of disinfection practices, the Agency believes it is important to evaluate these unregulated DBPs in the context of the review of the existing DBP regulations. DBPs need to be evaluated collectively, because the potential exists that the chemical disinfection used to control a specific DBP could affect the concentrations of other DBPs. Therefore, the Agency is not making a regulatory determination for chlorate and nitrosamines at this time."

Chlorate, like the related compound chlorite, is an oxidation state of chlorine. Chlorate and chlorite are chemically inter-convertible (see Chapter 6 for a detailed discussion.) They occur, and can co-occur, when hypochlorite solution and/or chlorine dioxide are applied during the drinking water treatment process. Chlorite is a regulated DBP (USEPA, 2016a). The potential common health effects and co-occurrence of chlorate and chlorite are discussed in the *Six-Year Review 3 Technical Support Document for Disinfectants/Disinfection Byproducts Rules* (USEPA, 2016a).

The remainder of this document provides a summary of available information and data relevant to EPA's understanding of the contaminant background, health effects, analytical methods, occurrence and exposure, formation and treatment/control strategies for chlorate. The information cutoff date for Six-Year Review 3 was December 2015. That is, information that was published after December 2015 was not considered for this document. The Agency recognizes that scientists and other stakeholders are continuing to investigate and publish relevant information subsequent to the cutoff date. While not considered as part of Six-Year Review 3, the Agency anticipates providing consideration of that additional information in subsequent activities.

2 Contaminant Background

This chapter presents background information on chlorate that EPA is evaluating under the SYR3 program. The following topics are covered in the chapter: physical and chemical properties; production, use and release; environmental fate; and regulatory and non-regulatory actions.

The chlorate anion (ClO₃⁻) forms a variety of salts (e.g., sodium chlorate, calcium chlorate, potassium chlorate and magnesium chlorate) that are collectively known as chlorates. Chlorate and its salts are powerful oxidizers. Sodium chlorate is registered for use as an herbicide and to generate chlorine dioxide for multiple uses, including bleaching paper and disinfecting drinking water (USEPA, 2006a). Disinfection practices are an important source of chlorate in drinking water; this includes formation as a disinfection byproduct (DBP) and presence in disinfectants as an impurity (USEPA, 2006a).

2.1 Chemical and Physical Properties

Exhibit 2.1 presents the structural formula for chlorate. Physical and chemical properties and other reference information are listed in Exhibit 2.2.

Exhibit 2.1: Chemical Structure of Chlorate



Source: ChemIDPlus/National Library of Medicine

Exhibit 2.2: Physical and Chemical Properties of Chlorate

Property	Data			
Chemical Abstracts Service (CAS) Registry Number	14866-68-3 (CAS registry number for "chlorates")			
EPA Pesticide Chemical Code	073301 (sodium chlorate), 073302 (calcium chlorate), 073303 (potassium chlorate), 530200 (magnesium chlorate)			
Chemical Formula	CIO3			
Molecular Weight	83.45 g/mol (Calculated)			
Color/Physical State	Colorless or white crystals (Lide, 1984)			
Boiling Point	Decomposes when heated above melting point (Lide, 1984)			
Melting Point	Varies with the salt (Lide, 1984); 248 deg C (NaClO ₃) (HSDB, 2015)			
Density	2.5 g/cm ³ (NaClO ₃) (HSDB, 2015)			
Freundlich Adsorption Coefficient				
Vapor Pressure	Negligible at room temperature (NaClO ₃) (HSDB, 2015)			
Henry's Law Constant				
Log Kow				
Koc				
Solubility in Water	1,000,000 mg/L @25°C (NaClO ₃) (HSDB, 2015)			
Other Solvents	Slightly soluble in ethanol (NaClO ₃) (HSDB, 2015)			

Note: "--" indicates that no information was found.

2.2 **Production**, Use and Release

2.2.1 Commercial Production and Use in Industry and Agriculture

According to Bommaraju and O'Brien (2015), most commercially-produced sodium chlorate (over 95 percent) is used to generate chemicals (e.g., chlorine dioxide) used for bleaching in the pulp and paper industry. The remainder is used in agriculture as an herbicide, in the manufacture of chlorites and potassium chlorate, in the hydraulic mining of uranium, and in the production of perchlorate for pyrotechnics, rocketry, and matchheads. Estimates of actual U.S. production and importation of both sodium chlorate and potassium chlorate, based on data gathered under EPA's Chemical Data Reporting (CDR) program, are presented below in Exhibit 2.3.

No industrial release data for chlorate or any of its salts are available from EPA's Toxics Release Inventory (TRI). (More precisely: the list of compounds for which TRI reporting is required has never included a compound with "chlorate" in its name (USEPA, 2016b)).

Sodium chlorate is approved for use on cotton, rice, corn, soybeans, dry beans, potatoes, sunflowers, flax, safflower, chili peppers, grain sorghum and wheat. It is also registered for use as a nonselective herbicide to kill grasses and weeds in industrial and non-agricultural sites such as uncultivated areas/soils and around ornamentals. There are 30 active product registrations containing sodium chlorate as an active ingredient (USEPA, 2016c). Data on the application of sodium chlorate compounds as a pesticide are available from several sources, as described in the

sections below. (No information about sodium chlorate usage was found in EPA's Pesticide Industry Sales and Usage Reports.)

2.2.1.1 Inventory Update Reporting (IUR) / Chemical Data Reporting (CDR) Program

In compliance with the Toxic Substances Control Act, EPA gathers information on the manufacturing (including both domestic manufacture and importation) of chemical substances. Under the Inventory Update Rule (IUR), manufacturers (including importers) provided information on a periodic basis between 1986 and 2006. Under the CDR Rule that superseded the IUR in 2011, manufacturers (including importers) are continuing to provide information once every four years (reporting under this rule began in 2012). CDR data gathered in 2012 cover reporting years 2010 and 2011.

Production data from EPA's CDR program are available for sodium chlorate and potassium chlorate for the years 2010 and 2011. No data on chlorate-related compounds are available from the IUR program in earlier years. Under CDR, the minimum reporting threshold was 25,000 pounds (USEPA, 2014b).

Eighteen industrial sites are reported as having "manufactured" (i.e., domestically manufactured or imported) sodium chlorate in both 2010 and 2011. The available data indicate that at least five of those sites domestically manufactured sodium chlorate, nine sites imported it, and one did both. Over 1.9 billion pounds were reported as manufactured each year in both 2010 and 2011. The actual quantities produced were likely higher, as some production figures were redacted as confidential business information. Reported per-facility imported quantities ranged from 0 to over 583 million pounds, and reported per-facility manufactured quantities ranged from 3.5 million to 311 million pounds.

There was no reported domestic manufacture of potassium chlorate in 2010 or 2011. Only one industrial site imported potassium chlorate, in quantities of 119,048 pounds in 2010 and 198,414 pounds in 2011.

Exhibit 2.3: Reported Annual Manufacture and Importation of Sodium Chlorate and Potassium Chlorate in the United States (pounds), from EPA's CDR Program

Contaminant	Type of Activity	Chemical Inventory Update Reporting Cycle (2010)	Chemical Inventory Update Reporting Cycle (2011)	
Sodium Chlorate	Domestic Manufacture	748,053,800	1,023,390,997	
Sodium Chlorate	Importation	730,746,281	913,070,966	
Sodium Chlorate	Total	1,936,490,474	1,936,461,963	
Potassium Chlorate	Domestic Manufacture	0	0	
Potassium Chlorate	Importation	119,048	198,414	
Potassium Chlorate	Total	119,048	198,414	

Source: USEPA, 2015a. Note: Because some reports do not specify whether production volumes represent manufacture or importation, values may not add up to totals.

2.2.1.2 National Center for Food and Agricultural Policy (NCFAP) Pesticide Use Database

The National Center for Food and Agricultural Policy (NCFAP) maintains a national Pesticide Use Database, primarily for herbicides. Pesticide use estimates are based on state-level commercial agriculture usage patterns and state-level crop acreage. NCFAP listed uses of sodium chlorate on six crops totaling approximately 8,293,000 pounds active ingredient per year in 14 states in 1992. In 1997, NCFAP listed uses of sodium chlorate on seven crops totaling approximately 7,262,000 pounds active ingredient per year in 16 states (NCFAP, 2009).

2.2.1.3 EPA Office of Pesticide Programs (OPP) Registration Review Program

In 2006, EPA's Office of Pesticide Programs (OPP) estimated that approximately 2.8 million pounds of sodium chlorate active ingredient were used annually in the United States (USEPA, 2006a). A 2015 screening level usage analysis covering the 2004-2013 timeframe indicated that approximately 1.2 million pounds of sodium chlorate were applied annually in agriculture, with the bulk applied to cotton and rice (USEPA, 2016d). This estimate does not include anti-microbial applications.

2.2.1.4 United States Geological Survey (USGS) Pesticide Use Maps

The United States Geological Survey (USGS) has produced maps of pesticide use for several hundred compounds used in United States crop production. The pesticide use maps show the average annual pesticide use intensity expressed as average weight (in pounds) of a pesticide applied to each square mile of agricultural land in a county. The USGS maps were created using data from NCFAP and county-level information on harvested crop acreage from the Census of Agriculture. The maps are complemented by bar graphs showing trends in total quantity applied annually, broken out by crop.

Exhibit 2.4 (USGS, 2015) shows the geographic distribution of estimated average annual sodium chlorate agricultural use in the United States in 2012. A breakdown of annual use by crop from 1992 to 2012 is presented in Exhibit 2.5. USGS used two methods to estimate sodium chlorate usage, since pesticide usage information was not available in some districts. On the left of Exhibit 2.4 and Exhibit 2.5, the "EPest-High" estimates were generated by projecting usage estimates for such districts based on usage in neighboring districts. On the right of Exhibit 2.4 and Exhibit 2.5, the "EPest-Low" estimates were generated by assuming no usage in such districts. According to these USGS estimates, annual usage peaked in the mid-1990s with a high of at least ~7.5 million pounds (in the low-usage estimate) of sodium chlorate. Since that time, annual use has exhibited a general decline, with approximately one million pounds having been applied annually in 2010, 2011 and 2012. The maps in Exhibit 2.4 indicate that the greatest use of sodium chlorate is in California, Arizona, Wisconsin and Georgia. Cotton is the major crop treated with sodium chlorate. (The anomalous spike in pasture and hay usage in 1996 appears to be an artifact of the "EPest-High" methodology.)



Exhibit 2.4: Estimated Annual Agricultural Use of Sodium Chlorate, 2012

Source: USGS, 2015

Exhibit 2.5: Estimated Annual Agricultural Use of Sodium Chlorate by Year and Crop, 2012



Source: USGS, 2015

2.2.2 Incidental Production and Release

Disinfection practices are an important source of chlorate in drinking water (USEPA, 2006a). The chlorate ion may be present as an impurity in sodium chlorite, the most common feedstock used to generate chlorine dioxide for drinking water treatment. Less frequently, chlorate compounds are used to generate chlorine dioxide for disinfection. Chlorate may persist and be carried through to finished water in either case. In addition, chlorate is one of a number of DBPs that can form during and after chlorine dioxide use in water treatment (USEPA, 2006a).

Chlorate may also be present as an impurity in hypochlorite solutions (sodium hypochlorite and calcium hypochlorite) used for drinking water disinfection. Concentrations of chlorate in hypochlorite solutions typically increase with storage time, and increase more quickly at higher temperatures. Chlorate may be introduced into water when the solutions are used for disinfection (Gordon et al., 1995; USEPA, 1999; USEPA, 2006a).

A report by the American Water Works Association Research Foundation (AwwaRF, since renamed the Water Research Foundation or WRF) (Gordon et al., 1995) found that chlorate concentrations in finished water were higher at facilities that use hypochlorite solutions for disinfection (mean concentration of 0.49 mg/L) than at facilities that use chlorine dioxide (mean concentrations of 0.25-0.29 mg/L). Additional information on the formation of chlorate during drinking water disinfection is presented in Chapter 6.

Chlorate may be present as an impurity or generated as a byproduct in other contexts as well. For example, just as it may be present in hypochlorite solutions used for drinking water disinfection as noted above, chlorate may also be present as an impurity in commercial sodium hypochlorite

used for cleaning, for pool disinfection and for medical and other uses. ICIS (2006) estimates that in 2005, 553 million gallons of household strength (5.25 percent) sodium hypochlorite and 310 million gallons of industrial strength (12.5 percent) sodium hypochlorite were used in the U.S. Use and disposal of this sodium hypochlorite could lead to the presence of chlorate in wastewater and the ambient environment.

2.3 Environmental Fate

Sodium chlorate is not expected to volatilize from soil or water, and sodium chlorate has low potential to bioaccumulate. Sodium chlorate is reported to persist in soil for 0.5 to 5 years, depending on soil type, application rate and weather conditions (USEPA, 2006a).

Chlorate salts readily dissolve in water. In the absence of redox reactions, the chlorate ion would be expected to partition predominantly into water and to be highly mobile in water. However, under most environmental conditions, chlorate is subject to redox reactions. Factors affecting oxidation and reduction in soil and water include temperature, pH, chlorate concentration, the nature and concentration of reductants, and the degree of moisture in soils. Alkaline conditions favor chlorate stability (USEPA, 2006a). As a strong oxidizing agent, chlorate is typically reduced to chlorine species in lower oxidation states, such as chloride. In the environment, extensive redox reactions are expected to reduce the concentration of chlorate in the water column (USEPA, 2006a).

2.4 Regulatory and Non-Regulatory Actions for Chlorate

Some domestic and foreign agencies have established regulatory actions or non-regulatory advisories to address chlorate contamination of drinking water.

In 2002, the State of California proposed an action level of 200 μ g/L for chlorate as a drinking water contaminant, based on a 20 percent relative source contribution (RSC) (CalEPA, 2002). Later, in 2007, the state set a notification level of 800 μ g/L, based on an 80 percent RSC (CDPH, 2007). The State of California maintained this level in 2015, with a note that chlorate may be produced during the disinfection process (CalEPA, 2015). Health Canada adopted an individual maximum acceptable concentration (MAC) (an enforceable standard) of 1 mg/L for chlorate and chlorite in 2008, based on an 80 percent RSC from drinking water (Health Canada, 2008). Using this MAC, NSF/ANSI 60 set a Single Product Allowable Concentration of 0.3 mg/L chlorate for products used in drinking water treatment (Stark, 2013).

The American Water Works Association (AWWA) conducted an assessment of the potential regulatory implications of chlorate in the United States in 2014, based on a health reference level of 210 μ g/L (AWWA, 2014). AWWA recommended that, even with uncertainties about potential future regulatory actions that might relate to chlorate, water systems might want to consider taking steps to better understand the levels of chlorate in their drinking water. The World Health Organization (WHO) set provisional guideline values (voluntary standards) of 0.7 mg/L each for chlorate and chlorite in 2005, using an 80 percent RSC, and requested public comments in 2015 (WHO, 2005, 2015). China adopted the WHO guideline values as its standards (Wang et al., 2015a).

3 Health Effects

This chapter presents a summary of chlorate health effects and derivation of the health reference level (HRL). As noted in Chapter 1, information about potential common health effects of chlorate and chlorite, as well as the disinfectant chlorine dioxide, is presented in the Six-Year Review 3 Technical Support Document for Disinfectants and Disinfection Byproducts Rules (D/DBPRs) (USEPA, 2016a).

3.1 Summary of Health Effects

Human oral data are available for chlorate from reports of poisoning incidents and clinical studies. Doses of >100 mg/kg of sodium chlorate are generally fatal in humans (USEPA, 2006b). The smallest dose of sodium chlorate reported to be fatal was 7,500 mg (107 mg/kg for a 70 kg adult), with two reports noting 10,000 mg (143 mg/kg for a 70 kg adult) as a fatal dose, and one report observing that "vigorous treatment saved one person who had ingested about 40,000 mg" sodium chlorate (USEPA, 2006b). Toxic doses of sodium chlorate can cause gastrointestinal irritation, hemolysis, methemoglobinemia, hemoglobinuria, disseminated intravascular coagulation, cyanosis and renal failure (WHO, 2005; USEPA, 2006b; Lee et al., 2013).

In a controlled clinical evaluation of chlorate (Lubbers et al., 1982, 1984), subjects ingesting a liter of water containing 0.01- 2.4 mg chlorate every third day for 16 days showed small but statistically significant changes in group means for serum bilirubin, iron and methemoglobin, which were within the normal range for each parameter.

Khan et al. (2005) conducted a short term study in male F344 rats that received daily doses of sodium chlorate for seven consecutive days. There was a dose-related decrease in the thyroid gland stores of thyroglobulin, the protein from which thyroid hormones are synthesized. The no observed adverse effect level (NOAEL) for this effect was 2.60 mg/kg/day chlorate and the lowest observed adverse effect level (LOAEL) was 12.3 mg/kg/day. Thyroid hormones have a shorter half-life in humans than in rats, making the rat more sensitive (Dohler et al., 1979). However, this study raises concerns for thyroid effects from short term chlorate exposures, especially when there is co-exposure to perchlorate. In the Khan et al. (2005) study, a mixture of 1.2 mg/kg/day chlorate combined with 0.9 mg/kg/day perchlorate resulted in both colloid depletion and a significant decrease in serum thyroxine. Chlorite is also associated with effects on thyroid hormones, with NOAELs that are higher (20 mg/kg/day, 30 mg/kg/day) than those seen for chlorate (Bercz et al., 1982; Orme et al., 1985). No mixture study of chlorate and chlorite on thyroid hormones was identified.

The major effects from subchronic and chronic exposure to sodium chlorate in animals are on the blood and thyroid. Subchronic studies in rats have reported decreased hemoglobin, hematocrit and red blood cell (RBC) counts (Abdel-Rahman et al., 1984; Barrett, 1987; McCauley et al., 1995). Severe thyroid colloid depletion, follicular cell hypertrophy and hyperplasia were reported in rats after 90-day exposures (Hooth et al., 2001). A chronic study (NTP, 2005) reported thyroid follicular cell hypertrophy and mineralization, as well as hyperplasia of the bone marrow in rats and hyperplasia of the bone marrow and granulosa cell hyperplasia of the ovary in

mice. These animal studies provide clear and consistent evidence that subchronic and chronic exposures to chlorate result in effects on the blood and thyroid.

The only long-term carcinogenicity study of chlorate in animals is a 2-year bioassay on sodium chlorate in drinking water in rats and mice (NTP, 2005). The National Toxicology Program (NTP, 2005) exposed male and female rats to 0, 125, 1,000, or 2,000 mg/L and male and female mice to 0, 500, 1,000, or 2,000 mg/L sodium chlorate for 2 years and concluded that there was 1) some evidence of carcinogenicity in male and female rats based on an increased incidence of thyroid gland neoplasms, 2) equivocal evidence of carcinogenicity in female mice based on marginally increased incidences of pancreatic islet neoplasms and 3) no evidence of carcinogenicity in male mice.

The chronic NTP (2005) study was identified as the critical study for establishing a reference dose (RfD) of 0.03 mg/kg/day for chlorate (USEPA, 2006b). The RfD was derived by using the Benchmark Dose (BMD) method and based on a Benchmark Dose Level (BMDL) of 28 mg/L as sodium chlorate (22 mg/L as chlorate) for increased follicular cell hypertrophy as the critical effect. The 22 mg/L concentration corresponds to a dose of 0.9 mg/kg/day for chlorate ion (USEPA, 2006b). A net uncertainty factor (UF) of 30 was applied when deriving the RfD. This consisted of a UF of 10 for inter-human variability for potentially sensitive individuals in the absence of information on the variability of response in humans and a UF of 3 for interspecies uncertainty because there is increased activity of the thyroid-pituitary axis in rats (Döhler et al., 1979; McClain, 1992) modulating the applicability of the thyroid effects in rats when extrapolated to humans. A UF of 1 was assigned for LOAEL-to-NOAEL adjustment because the BMDL approach was used to set the RfD; a UF of 1 for subchronic to chronic extrapolation because a chronic study was used; and a UF of 1 for database uncertainties because the database of chlorate includes subchronic, chronic, developmental and reproductive studies.

Sodium chlorate is classified as "not likely to be carcinogenic to humans at doses that do not alter thyroid hormone homeostasis" (USEPA, 2006b). This classification is in accordance with the EPA policy, Assessment of Thyroid Follicular Cell Tumors (USEPA, 1998), which states that nonmutagenic pesticides that induce elevated levels of thyroid-stimulating hormone (TSH) and follicular cell tumors in rats are classified as not likely to be carcinogenic to humans at doses that do not alter thyroid hormone homeostasis (USEPA, 2006b). Sodium chlorate is considered to be nonmutagenic based on negative results in most *in vitro* and *in vivo* gene mutation assays, including gene mutation tests in bacteria and Chinese hamster lung cells, and tests of micronuclei and chromosomal damage in mouse bone marrow (USEPA, 2006b). A quantitative cancer risk assessment was not conducted for chlorate because sodium chlorate is classified as likely to be carcinogenic to humans at doses that disturb thyroid homeostasis but not likely at doses that do not. Thus, protection provided by the RfD will also be protective for cancer.

EPA also evaluated whether health information is available regarding potential effects on children and/or other sensitive populations. There was no pre- or post-natal sensitivity or susceptibility observed in developmental studies of sodium chlorate in rats and rabbits, including a two-generation reproduction study in rats. However, evidence suggests that there may be a concern for developing offspring because of the effects of inorganic chlorate on thyroid function in rats (USEPA, 2006b). Chlorate is one of a number of inorganic ions that can interfere with iodine uptake by the thyroid, but chlorate is not highly potent in this respect (Van Sande et al., 2003).

Chlorate is able to cause hemolysis at doses greater than the RfD. Thus, persons with low RBC counts, such as those with anemia, may be particularly sensitive to sodium chlorate. However, it is not clear whether the fetus or newborn is more sensitive to the hemolytic effect of chlorate than adults (CalEPA, 2002) because of age alone. Data from the 1994 National Health Interview Survey (O'Day et al., 1998) indicate that there were about 5 million people in the U.S. who suffered from some form of anemia. About 3 to 5 percent of the population may have an inherited glucose-6-phosphate dehydrogenase (G6PD) deficiency increasing their risk for methemoglobinemia, with males more sensitive than females (Luzzatto and Mehta, 1989). Additionally, about 1 percent may have a form of hereditary methemoglobinemia (Jaffe and Hultquist, 1989). Each one of these conditions is a contributor to low RBC counts within the population, which renders them more sensitive to chlorate than the general population. Individuals co-exposed to other ions that decrease iodine uptake by the thyroid (e.g., perchlorate) or cause methemoglobinemia and low RBC counts (e.g., nitrate or nitrite) could be more sensitive to chlorate exposure (Khan et al., 2005) than the general population.

3.2 Derivation of the Health Reference Level

To evaluate the systems and populations exposed to chlorate in drinking water from public water systems (PWSs), monitoring data were compared to a concentration in drinking water that is termed the health reference level (HRL). The HRL is a risk-derived concentration against which to compare the occurrence data from PWSs to determine if chlorate occurs with a frequency and at levels of public health concern. HRLs are not final determinations about the level of a contaminant in drinking water that is necessary to protect any particular population and they are derived prior to development of a complete exposure assessment.

EPA calculated a long-term non-cancer HRL of $210 \mu g/L$ for chlorate, using the RfD of 0.03 mg/kg/day for a 70-kg adult ingesting 2 L of drinking water per day and a default relative source contribution (RSC) of 20 percent (USEPA, 2014a). The agency anticipates evaluating health effects related to short-term exposures as part of potential future regulatory actions. EPA derived the HRL for chlorate using the RfD approach as follows:

HRL (mg/L) = $[(RfD \times BW)/DWI] \cdot RSC$

Where:

- RfD = Reference Dose (mg/kg/day)
- BW = Body Weight for an adult, assumed to be 70 kilograms (kg); for a child, assumed to be 10 kg
- DWI = Drinking Water Intake for an adult, assumed to be 2 L/day (90th percentile); for a child, assumed to be 1L/day (90th percentile)
- RSC = Relative Source Contribution, or the level of exposure believed to result from drinking water when compared to other sources (e.g., food, ambient air). In the absence of a complete exposure assessment, a default RSC value is used in the calculation of the HRL. Default values are based on the Exposure Decision Tree (USEPA, 2000). 20 percent is the most conservative RSC used in the derivation of a maximum contaminant level goal (MCLG) for drinking water.

Chlorate is introduced into the food supply when tap water containing chlorate is used for food preparation, when crops are treated with sodium chlorate as an herbicide, and when chlorine dioxide and/or hypochlorites are used as disinfectants by the food industry (USEPA 2006a, 2006b; WHO, 2008; Asami et al., 2013).

The RfD for chlorate is protective against acute alterations in thyroid homeostasis and, therefore, considered to also be protective of tumorigenicity as well as other chronic and subchronic adverse health effects discussed in the literature (Hooth et al., 2001; Khan et al., 2005; NTP, 2005).

3.2.1 Considerations of Relative Source Contribution (RSC) from Drinking Water for Chlorate

The following data sources could be useful in deriving an RSC for chlorate following the EPA decision tree approach (USEPA, 2000):

- The Office of Pesticide Programs Reregistration Eligibility Decision for inorganic chlorates as pesticides applied to a variety of crops and in antimicrobial applications, and related documentation (USEPA, 2006a, 2006b, 2016c);
- Monitoring data from the Third Unregulated Contaminant Monitoring Regulation (UCMR 3) from the water treatment plants and within the distribution system;
- A well designed total diet study that analyzed the levels of chlorate in foods prepared with distilled water and in foods prepared with tap water containing a known amount of inorganic chlorate (Asami et al., 2013). Although the study was carried out in Japan, it is possible to harmonize the data using food group consumption data from the U.S., Continuing Survey of Food Intakes by Individuals in the United States (CSFII);

• A published study on the levels of chlorate in dietary supplements and flavor enhancers (Snyder et al., 2006).

3.3 Additional Perspective on Chlorate in DBP Mixtures from Epidemiology Studies

Righi et al. (2012) conducted a case-control study in Northern Italy to investigate the relationship between drinking water exposure to chlorite, chlorate and trihalomethanes (THMs) and congenital anomalies. A total of 1,917 cases of congenital anomalies (neural tube, cardiac, diaphragm and abdominal wall, esophagus (food pipe or gullet), cleft lip and palate, respiratory, urinary tract and chromosomal anomalies) observed in the period of 2002 to 2005 were studied. The THM exposure levels were reported to be very low (mean $3.8 + 3.6 \mu g/L$), and no excess risk of anomalies were associated with THM exposures. The levels of chlorite (mean 427 + 184 $\mu g/L$) and chlorate (mean 283 + 79 $\mu g/L$), however, were relatively high. The authors reported that women exposed to chlorite at levels > 700 μ g/L were at higher risk of having newborns with renal defects (OR: 3.30; 95 percent CI: 1.35-8.09), abdominal wall defects (OR: 6.88; 95 percent CI: 1.67-28.33) and cleft palate (OR: 4.1; 95 percent CI: 0.98-16.8); women exposed to chlorate at levels $>200 \mu g/l$ were at higher risk of newborns with obstructive urinary defects (OR: 2.88; 95 percent CI: 1.09-7.63), cleft palate (OR: 9.60; 95 percent CI:1.04-88.9) and spina bifida (OR: 4.94; 95 percent CI:1.10-22). The authors noted that this was the first study showing an excess risk of different congenital anomalies associated with chlorite and/or chlorate exposure from drinking water, and that further research using larger datasets was needed to confirm the observed results.

In an earlier population-based, case-control study from the same area, Aggazzotti et al. (2004) examined the association between chlorination byproducts and adverse pregnancy outcomes. The chlorination byproducts investigated in this study were chlorate and chlorite and total and individual THMs: chloroform, dichlorobromomethane, dibromochloromethane and bromoform. A total of 1,194 subjects were evaluated in the study, consisting of 343 pre-term (<37 weeks) births, 239 full-term small for gestational age (SGA) births (< 10th percentile of birth weight according to standard values from the Italian Society of Pediatrics) and 612 controls (born \geq 37 weeks and $\geq 10^{\text{th}}$ percentile of birth weight). Exposure was assessed both by a questionnaire completed by the mothers on their personal habits during pregnancy and by water samples collected at the homes of the participants. The median concentrations of chlorate for pre-term births, full-term births and controls were: 76.20, 72.0 and 76.5 µg/L, respectively. No association was found between pre-term births and exposure to chlorate or to any of the other chlorination byproducts studied. For a subgroup of 59 term-SGA cases and 113 controls having "high exposure" to THMs (\geq 30 µg/L), chlorite (\geq 200 µg/L) or chlorate (\geq 200 µg/L), a weak association was found (OR: 1.38; 95 percent CI: 0.92-2.07). However, separate analyses for exposure to high levels of THMs, chlorite or chlorate individually showed a relationship between term-SGA and high chlorite exposure but not for high THM or high chlorate exposure (the authors note that there was a small number of subjects exposed to high levels of chlorate that could be a limitation for that analysis).

4 Analytical Methods

EPA has developed four analytical methods that are available for the analysis of chlorate in drinking water:

- EPA Method 300.0, Revision 2.1, *Determination of Inorganic Anions by Ion Chromatography*, reported a Method Detection Limit (MDL) of 3 µg/L. Reagent water and finished drinking water samples fortified with 0.05 to 5 µg/L chlorate yielded recoveries that ranged from 97 to 121 percent (USEPA, 1993);
- EPA Method 300.1, Revision 1.0, *Determination of Inorganic Anions in Drinking Water by Ion Chromatography*, reported MDLs that range from 0.78 to 2.55 µg/L. Reagent water and finished drinking water samples fortified at 100 and 500 µg/L chlorate yielded recoveries that ranged from 86.1 to 106 percent, and percent Relative Standard Deviations (percent RSDs) of 0.47 to 2.14 percent (USEPA, 1997);
- EPA Method 317.0, Revision 2.0, Determination of Inorganic Oxyhalide Disinfection By-Products in Drinking Water Using Ion Chromatography with the Addition of a Postcolumn Reagent for Trace Bromate Analysis, reported MDLs that range from 0.62 to 0.92 µg/L. Reagent water and finished drinking water samples fortified at 100 and 500 µg/L chlorate yielded recoveries that ranged from 86.1 to 106 percent, and percent RSDs of 0.47 to 2.14 percent (USEPA, 2001). Note that the recovery and RSD data are identical to the recovery and RSD data from EPA Method 300.1;
- EPA Method 326.0, Revision 1.0, Determination of Inorganic Oxyhalide Disinfection By-Products in Drinking Water Using Ion Chromatography Incorporating the Addition of a Suppressor Acidified Postcolumn Reagent for Trace Bromate Analysis, reports a Detection Limit (DL) of 1.7 µg/L. Reagent water and finished drinking water samples fortified at 100 and 500 µg/L chlorate yielded recoveries that ranged from 99.0 to 111 percent, and percent RSDs of 0.66 to 2.8 percent (USEPA, 2002).

ASTM International Method D6581-08 and Standard Method (SM) 4110 D are two additional, for-purchase voluntary consensus standard organization analytical methods. Both methods were approved for chlorate monitoring under the third cycle of the Unregulated Contaminant Monitoring Rule (UCMR 3). ASTM D6581-08 has an operational range for chlorate of 5-500 μ g/L (using chemically-suppressed ion chromatography) and an operational range for chlorate of 20-1,000 μ g/L (using electrolytically suppressed ion chromatography). ASTM International indicates that Method D6581-08 is "technically equivalent with Part B of U.S. EPA Method 300.1" (ASTM, 2008). ASTM Method D6581-08 reported an MDL for the electrolytic suppression portion of the method of 0.32 μ g/L in reagent water. Finished drinking water samples from eight ground water or surface water sources fortified at 20, 25, 180, 220, 400 and 450 μ g/L chlorate yielded mean recoveries that ranged from 93 to 107 percent for the electrolytic suppression portion of the method.

SM 4110 D in the 21st edition of SM, published in 2005, was approved for monitoring chlorate under UCMR 3 (USEPA 2012; 77 FR 26072). The data reviewed was obtained from SM 4110 D in the 22nd edition of SM (SM, 2012). The reported MDL, fortified reagent water and fortified finished drinking water recoveries, and percent RSDs for SM 4110 D are identical to those published by EPA in EPA Method 300.1 (USEPA, 1997).

Although not listed in any of the EPA methods, the Minimum Reporting Level (MRL) for chlorate was established at 20 μ g/L and served as a national benchmark for laboratories that participated in UCMR 3 using EPA Method 300.1 (USEPA, 2012; 77 FR 26072).¹

Estimated reporting levels for EPA Method 300.0, Rev. 2.1; 317.0, Rev. 2.0; and 326.0, Rev. 1.0 (calculated as five times the MDL or DL) and the MRL for EPA Method 300.1, Rev. 1.0 were compared to the Health Reference Level (HRL) for chlorate to determine whether the available analytical methods are capable of reliable quantitation at concentrations of estimated toxicological concern (see Exhibit 4.1). The Method Sensitivity Ratio (MSR) is calculated from the following equation:

MSR = HRL (μ g/L) / MRL or 5x the MDL or DL (μ g/L)

A favorable MSR is one that is greater than ten. That is, it is preferable that the HRL be at least ten times above the concentration at which data can be reliably reported; this provides a margin of safety for uncertainty in the HRL and/or method performance (USEPA, 2009a).

Method	MDL or DL (µg/L)	5x the MDL or DL (μg/L)	MRL (µg/L)	HRL (μg/L)	MSR
300.0, Rev. 2.1	3	15		210	14
300.1, Rev. 1.0 ¹			20	210	10.5
317.0, Rev. 2.0	0.62-0.92	3.1-4.6		210	45.6-67.7
326.0, Rev. 1.0	1.7	8.5		210	24.7

Exhibit 4.1: Method Sensitivity Ratios (MSRs) for Chlorate

¹ Since ASTM D6581-08 and SM 4110 D are based on EPA Method 300.1, the MSRs for these two methods are anticipated to be similar to the MSR calculated for EPA Method 300.1.

For all of the methods tabulated in Exhibit 4.1, the MSRs are greater than ten; hence, the available analytical methods should be capable of reliable quantitation at least ten times below the HRL. Note that EPA Method 317.0, Rev. 2.0 has performance options that result in higher MDLs; however, use of the other method options also results in favorable MSRs.

¹ At the time of Rule publication, then-most-recent versions of ASTM D6581-08 and SM 4110 D (21st edition) were listed as allowed alternative methods to EPA Method 300.1 for UCMR 3 monitoring (USEPA, 2012).

Additional potential analytical methods that are not approved by EPA for the analysis of drinking water for chlorate have been identified in the literature. In particular, two methods that are based on liquid chromatography and tandem mass spectrometry (LC-MS/MS) have been evaluated relative to EPA Method 300.1. Stanford et al. (2013) documents a comparison of four laboratories performing oxyhalide analyses using three analytical methods. Two of the laboratories utilized EPA Method 300.1, one laboratory utilized the LC-MS/MS method of Li and George (2005) (presumably adapted for the determination of chlorate), and the fourth laboratory utilized the LC-MS/MS method of Pisarenko, et al. (2010). As reported in Stanford et al. (2013), the LC-MS/MS method of Li and George (2005) demonstrated somewhat lower recoveries of chlorate than those obtained from two laboratories utilizing EPA Method 300.1. The fourth laboratory, using the LC-MS/MS method of Pisarenko et al. (2010), obtained chlorate recoveries that were more comparable to the results from the two laboratories that utilized EPA Method 300.1, although the results using the method of Pisarenko et al. (2010) were sometimes biased slightly high. The lack of a stable, isotopically-labelled chlorate standard (i.e., $Cl^{18}O_3^{-1}$) and a resultant sensitivity to matrix interferences were cited as the reasons for the low bias observed in the results from the method of Li and George (2005) (Stanford et al., 2013).

5 Occurrence and Exposure in Drinking Water

This section presents and discusses information about the occurrence and exposure to chlorate in drinking water from public water systems (PWSs). The best data available for chlorate occurrence in finished drinking water in PWSs are from the nationally representative monitoring completed under the third round of the Unregulated Contaminant Monitoring Rule (UCMR 3). The UCMR 3 monitoring provides nationally representative contaminant occurrence data for chlorate and other contaminants in the United States. The UCMR 3 program took place from 2012 to 2016. Most of the monitoring was conducted between 2013 and 2015. Gathering and reporting of some data continued in 2016. Additional sources of information about the occurrence of chlorate include the EPA's 1996 Disinfection Byproducts Rule Information Collection Rule (DBP ICR) (USEPA, 1996; 61 FR 24353), EPA's Community Water System Survey (USEPA, 2009b) and the Environmental Working Group Drinking Water Database (EWG, 2015). These additional data sources are summarized in Appendix A of this document.

As indicated in Chapter 2, chlorate may be released to the environment from commercial production and use and other sources. National data on chlorate occurrence in ambient water are not available. Limited chlorate ground water monitoring data from various sources are reported in the federal government's Water Quality Portal (<u>http://www.waterqualitydata.us/portal/</u>). Because these data are sparse and expected to be of mixed quality, EPA did not review them in detail for the Third Six-Year Review effort. As presented and discussed below, chlorate occurrence in undisinfected ground water (GW) systems could imply chlorate contamination in the source water.

As described in Chapter 3, a Health Reference Level (HRL) of 210 μ g/L was calculated for chlorate based on a chronic study for long-term non-carcinogenic effects, identified as the critical study. Occurrence data in finished drinking water from the UCMR 3 presented below are compared to the HRL, twice the HRL (420 μ g/L) and three times the HRL (630 μ g/L). As appropriate, estimates of the population exposed at concentrations above these thresholds are also presented.

National occurrence and exposure are estimated and discussed for both individual sampling results and locational averages. Note that the average concentrations are more relevant than the levels in individual samples in an evaluation of the long-term exposure effects of chlorate. Thus, in order to characterize national occurrence of and exposure to chlorate, EPA used the UCMR 3 data to calculate the average concentrations at each location (both the entry points (EPs) and the location of maximum residence (MR) time within the distribution system). Appendix B.2 presents the analytical results based on individual chlorate samples. The UCMR 3 data are also analyzed in order to understand: (1) chlorate occurrence by disinfectant type and system size, (2) spatial variation of chlorate occurrence from the EPs to the MRs and (3) changes in chlorate occurrence over time. Appendix B.4 contains the analytical results pertaining to the disinfectants used nationally during the UCMR 3 monitoring period. Appendix B.5 discusses the analyses of UCMR 3 data conducted to improve the understanding of the impact of changes in disinfectant types nationally. For information on the co-occurrence of chlorate and chlorite, refer to the *Six-Year Review 3 Technical Support Document for Disinfectants/Disinfection Byproducts Rules* (USEPA, 2016a).

5.1 UCMR 3 Monitoring Program and Dataset

The purpose of EPA's unregulated contaminant monitoring program is to collect data on the occurrence of contaminants suspected to be present in drinking water, but that do not have established health-based national standards under the Safe Drinking Water Act. UCMR 3 monitoring, conducted between 2013 and 2016, provides the data for the chlorate occurrence analysis presented in this section. The latest version of this dataset is available from the Agency's website (https://www.epa.gov/dwucmr/occurrence-data-unregulated-contaminant-monitoring-rule).

Similar in design to UCMR 1 and UCMR 2, UCMR 3 involves multiple tiers of monitoring: Assessment Monitoring for contaminants with commonly used analytical method technologies (including methods for chlorate), Screening Survey monitoring for contaminants that require specialized analytical method technologies not in wide or common use, and Pre-Screen Testing for contaminants that require analysis with methods that use new or specialized technology. Chlorate was part of the Assessment Monitoring and underwent monitoring using EPA Method 300.1. The minimum reporting level (MRL) used for chlorate in the UCMR 3 survey was 20 μ g/L.

For UCMR 3 Assessment Monitoring, all large (serving between 10,001 and 100,000 people) and very large (serving more than 100,000 people) community water systems (CWSs) and nontransient non-community water systems (NTNCWSs), plus a statistically representative national sample of 800 small PWSs (serving 10,000 people or fewer), were required to participate. Surface water (and ground water under the direct influence of surface water (GWUDI)) sampling locations were monitored four times during the applicable year of monitoring, and ground water sample locations were monitored twice during the applicable year of monitoring. Monitoring for chlorate was conducted at two types of sampling locations: the EP and MR locations. UCMR 3 also required that the participating systems indicate which MR location(s) were associated with each EP location. (Note that in some cases, multiple EP locations could be associated with a single MR location.) Furthermore, the UCMR 3 required PWSs to report the type of disinfectant in use at the time of sampling for each EP and MR location and for each sampling event. See the Federal Register (USEPA, 2012; 77 FR 26072) for more information on the UCMR 3 study design.

The design of UCMR 3 enables estimates of national occurrence. The UCMR 3 monitoring collects occurrence data from the survey of small systems that can be used to extrapolate national occurrence. To calculate national extrapolations, the percent of systems (or population served) estimated to exceed a specified threshold can be multiplied by the total number of systems (or population served) in the nation. In UCMR 3 analysis, the extrapolation methodology is applied only to small systems. Because all large and very large systems were required to participate in the UCMR 3 Assessment Monitoring, the data collected by systems in these size categories represent a census of systems and therefore directly represent national occurrence. (They do not require national extrapolation.) Total national occurrence is then estimated by adding the extrapolated national values of small systems to the census values of the large and very large system size categories.

The UCMR 3 occurrence analyses presented in this report for chlorate are based on data collected through May 2016 and released in July 2016 (USEPA, 2016e). EPA expects a relatively small amount of data reporting to continue after July 2016. The UCMR 3 dataset will not be considered "final" until early 2017. The final numbers will be presented and analyzed in a future report by EPA. EPA does not anticipate that there will be any substantial difference between findings based on the July 2016 data set and findings based on the final data set.

Exhibit 5.1 presents a comparison of the number of UCMR 3 systems expected to submit data with the number of systems that have submitted UCMR 3 chlorate data as of July 2016. Through July 2016, data had been received from 98 percent of systems that are expected to submit UCMR 3 chlorate data. About 94 percent of the 4,908 systems with chlorate data had submitted 100 percent of expected data as of July 2016. (Expected data include two samples per ground water sample location and four samples per surface water sample location during a 12-month period.)

Exhibit 5.1. Comparison of the Number of Systems in the UCMR 3 Sample Design with the Number of Systems with Chlorate Data in UCMR 3 Data

System Size	Expected Number of UCMR 3 Systems	Systems That Have Submitted Chlorate Data (as of July 2016)	Percent of Expected Systems	
Small Systems (≤10,000)	800	799	99.9%	
Large Systems (10,001-100,000)	3,780	3,701	97.9%	
Very Large Systems (>100,000)	411	408	99.3%	
Total	4,991	4,908	98.3%	

Source: USEPA, 2016e

It is also important to note that both CWSs and NTNCWSs monitored for chlorate under UCMR 3 and results from both system types are included in the analyses below. With both CWSs and NTNCWSs included in the analysis, there can be concern about over-estimating exposure by double-counting individuals who consume drinking water at home (via a CWS) and at workplaces or schools (via NTNCWSs). Exhibit 5.2 presents a breakdown of the count of records for these two system-type categories. A very small percentage of the chlorate data were submitted by NTNCWSs (specifically, less than one percent of the number of samples and approximately 2 percent of systems serving only 0.3 percent of the overall population served by participating systems). Thus, it is not expected that the occurrence analyses below will significantly overestimate potential exposure estimates with the inclusion of both CWS and NTNCWS data. Additional UCMR 3 analyses based on CWS data only and NTNCWS data only are included in Appendix B.1 (i.e., Exhibit B.1 through Exhibit B.4).

System Type ¹	Number of Samples	% of Total Samples	Number of Systems	% of Total Systems	Population Served by Systems	% of Total Population Served by Systems
Community Water Systems	61,871	99.1%	4,805	97.9%	240,108,699	99.7%
Non-Transient Non- Community Water Systems	543	0.9%	103	2.1%	685,183	0.3%
Total	62,414	100%	4,908	100%	240,793,882	100%

Exhibit 5.2. UCMR 3 Chlorate Data, By System Type

Source: USEPA, 2016e.

¹ System type information was not included in the download of the UCMR 3 data in July 2016. The UCMR 3 data were linked with information from the Safe Drinking Water Information System / Federal version (SDWIS/Fed) database (December 2010) to identify the system type of each water system.

Note also that the July 2016 version of the UCMR 3 data (USEPA, 2016e) did not include the source water type or the population served by each public water system identification number (PWSID) with data. For the various occurrence analyses presented in this report, the data set used by EPA (provided by EPA's Technical Service Center (TSC)) included the source water type and population served information for each PWSID in the UCMR 3 sample design inventory. This file also made it possible for EPA to assess the completeness of the July 2016 version of the UCMR 3 data included in Exhibit 5.1.

5.2 Summary of Analytical Results with UCMR 3 Data

Extrapolation of the analytical results on locational averages based on the UCMR 3 data suggests that an estimated 25,000 sampling locations (17 percent of sampling locations nationally) serving almost 52 million people nationally would have average chlorate concentrations above the HRL, an estimated 10,000 sampling locations (7 percent) serving 15 million people nationally would have average concentrations above twice the HRL and an estimated 5,100 sampling locations (3 percent) serving almost 6 million people nationally would have average concentrations above the HRL and an estimated 5,100 sampling locations (3 percent) serving almost 6 million people nationally would have average concentrations above three times the HRL.

UCMR 3 findings show that some disinfection techniques are associated with relatively high chlorate occurrence. The disinfection techniques using bulk hypochlorite solution and on-site generated (OSG) hypochlorite were associated with more chlorate detections (87.6 percent and 78.4 percent, respectively) than gaseous chlorine (16.3 percent). Chlorine dioxide is also associated with elevated chlorate concentrations: 90.1 percent of samples where chlorine dioxide was used had detectable levels of chlorate. These observations are consistent with the formation information presented and discussed in Chapter 6 of this document. Note that chlorate was detected in 22.3 percent of samples where no disinfectant was in use (mostly these samples were at GW systems), thus implying chlorate contamination of source waters. Pesticides are a possible source of source water contamination (see Chapter 2).

For a given disinfectant type (such as chlorine dioxide or hypochlorite), small systems in general have higher chlorate levels than large systems. There are several factors that could contribute to this trend, including higher doses of disinfectants or longer storage times in small systems.

A comparison of paired chlorate results (i.e., samples that were collected at an EP sampling location and at a corresponding MR sampling location) shows that chlorate concentrations at MR sampling locations tend to be slightly higher than concentrations at EP sampling locations. This is true when all paired results are considered, and also when the subsets of paired results associated with chlorine dioxide or with hypochlorite, respectively, are considered. More than half of all paired samples had a higher chlorate concentration at the MR location than at the EP location. There is wide variability in the differences between MR and EP concentrations among the UCMR 3 systems.

The data collected between 2013 and 2016 under the UCMR 3 show approximately twice the percentage of samples with chlorate concentrations greater than the HRL compared to samples based on the data from the 1998 DBP ICR among common systems using chlorine dioxide or hypochlorite.

5.3 Occurrence and Exposure Based on UCMR 3 Locational Average Concentrations

As described earlier, EPA conducted an analysis based on annual average concentrations at each sampling location (including results from both EP and MR sampling locations) to relate the long-term exposure in context of different chlorate thresholds (including HRL, 2xHRL, and 3xHRL). These annual averages, based on up to one year of data per sampling location, are somewhat similar to the locational running annual averages (LRAAs) that are the basis for compliance monitoring for certain disinfection byproducts (DBPs) under the Microbial and Disinfection Byproduct (MDBP) rules. However, since UCMR 3 requires participating systems to gather only two or four samples per sampling location over the course of one year (two in the case of ground water sampling locations, four in the case of surface water sampling locations), a "running annual average" was not calculated. Averages were calculated for all individual sampling locations included in the UCMR 3 dataset, regardless of whether or not sampling was complete (e.g., ground water sampling locations with fewer than two samples or surface water sampling locations with fewer than four samples). Non-detections were assigned a value of zero.

For the purpose of calculating population exposure, each system's population was assumed to be equally distributed among its several sampling locations. With this assumption, the population served by a sampling location with an average concentration of chlorate above a given threshold is calculated by multiplying the system's total population served by the fraction of sampling locations with an average concentration of chlorate above that threshold.

National estimates based on this LRAA analysis (Exhibit 5.3) suggests that approximately 25,000 sampling locations, serving 52 million people, may have average chlorate concentrations above the HRL; an estimated 10,000 sampling locations, serving 15 million people, may have average concentrations above twice the HRL; and an estimated 5,100 sampling locations, serving 6 million people, may have average chlorate concentrations above three times the HRL. Additional analyses on locational averages based on the UCMR 3 data are included in Appendix B.3.

Exhibit 5.3: National Estimates of Sample Locations and Associated Population Served with Locational Average Chlorate Concentrations Greater than Threshold Values (Based on UCMR 3 Data)

Threshold Concentration	National Estimate of Number of Sample Locations with Locational Average Concentration > Threshold (Percent ¹)	National Estimate (in million) Population Served by Sample Locations with Locational Average Concentration > Threshold (Percent ¹)
> HRL (210 µg/L)	24,868 (16.59%)	52 (17.43%)
> 2xHRL (420 µg/L)	10,168 (6.78%)	15 (5.06%)
> 3xHRL (630 µg/L)	5,124 (3.42%)	6 (2.00%)

Source: UCMR 3 chlorate data available in July 2016 (USEPA, 2016e).

¹ The estimated percentages of the national population exceeding the thresholds shown in this table are slightly different from the percentages of the UCMR 3 sample population exceeding the thresholds (which are shown in Exhibit B.16 through Exhibit B.18), reflecting the fact that the small systems are only a sample whereas the larger systems are taken as a census. These percentages are calculated by dividing the nationally estimated/extrapolated count of systems/sampling locations/population served with threshold exceedances by the national inventory number of systems/sampling locations/population served.

5.4 Occurrence by Disinfectant Type

As discussed in Section 2.2.2 (above) and Chapter 6 of this document, chlorate occurrence is expected to vary among PWSs depending on disinfectant types employed. The UCMR 3 database provides a comprehensive set of information available about disinfectant use in the U.S. Under the UCMR 3, disinfectant type is identified for specific monitoring locations (EP or MR) rather than at a system-level. The disinfectant type for a given monitoring period was specific to that monitoring location rather than to the system as a whole. As such, inferences about system-level disinfectant use for a given year may tend to overestimate use of a type of disinfectant in situations where that disinfectant was only used for a portion of the UCMR 3 monitoring program.

Disinfectant type codes in the UCMR 3 database enable EPA to evaluate patterns in chlorate occurrence. The following eleven disinfectant designation codes are used in the UCMR 3 database. If more than one disinfectant is used simultaneously, a sample may be associated with more than one disinfection designation. Disinfection designations may also vary from one sample to another at the same sampling location if, for example, disinfection practices change over time.

- CLGA (gaseous chlorine),
- CLOF (off-site generated hypochlorite stored as liquid),
- CLON (on-site generated hypochlorite with no storage),
- CAGC (chloramine formed from gaseous chlorine),
- CAOF (chloramine formed from off-site hypochlorite),

- CAON (chloramine formed from on-site hypochlorite),
- CLDO (chlorine dioxide),
- OZON (ozone),
- ULVL (ultraviolet light),
- OTHD (all other types of disinfectant),
- NODU (no disinfection).

Off-site generated hypochlorite liquid is frequently referred to as "bulk" hypochlorite solution. The abbreviation "OSG" is sometimes used to refer to on-site generated hypochlorite. Those conventions will be followed in this document.

Note that the disinfection data in the database are "as reported" and did not undergo independent verification or quality assurance review. There are numerous blank disinfectant designation fields: approximately 18 percent of chlorate samples in the UCMR 3 database (July 2016 version) are associated with no disinfectant designation. In addition, more than 250 surface water chlorate samples were reported as using no disinfection (NODU); this is presumably due to incorrect self-reporting, as disinfection is required for all surface water systems. These NODU records came from 52 different water systems.

Exhibit 5.4 through Exhibit 5.8 present results (including reported detections, exceedances of the HRL (210 μ g/L), exceedances of twice the HRL (420 μ g/L) and exceedances of three times the HRL (630 μ g/L)) in individual chlorate samples under various disinfection scenarios. Exhibit 5.4 compares results under three exclusive chlorination scenarios (gaseous chlorine, OSG hypochlorite and bulk hypochlorite solution). Exhibit 5.5 presents a comparison between results under the three chlorination scenarios and results under three parallel chloramination scenarios. Exhibit 5.6 presents results for all samples associated with the chlorine dioxide code, as well as chlorine dioxide in combination with each of the three forms of chlorination. In a similar format, Exhibit 5.7 and Exhibit 5.8 present results for ozonation and ultraviolet light, respectively. Exhibit 5.8 also presents results associated with any "other disinfectant" and results clearly designated as associated with no disinfectant.

To generate the counts of EPs and MRs in Exhibit 5.4 through Exhibit 5.9 (as well as Exhibit B.19 through Exhibit B.23), two data tables from the UCMR 3 data set ("UCMR3_All" and "UCMR3_DRT") were linked. The "UCMR3_All" table contains all of the UCMR 3 data (i.e., sample analytical results as of July 2016); the "UCMR3_DRT" table contains the disinfectant residual type information for all of the UCMR 3 results (as of July 2016). These two tables were linked on the public water system identification code, facility identification code, sample point identification code, sample event code, and sample collection date (i.e., PWSID, FacilityID, SamplePointID, SampleEventCode, and CollectionDate) to identify the disinfectant residual type was specified for a particular water system. There were also situations where more than one disinfectant residual type was specified for a particular sampling location / sample event. Such

cases were consolidated so that there were multiple disinfection codes corresponding to a unique sampling location / sample event. Thus, multiple disinfection codes in Exhibit 5.4 through Exhibit 5.9 (as well as Exhibit B.19 through Exhibit B.23), could reflect simultaneous use of multiple disinfectants or changes in disinfection practices over time.

In the exhibits below, a graphical system is used in the column headings to clarify which combinations of disinfectant codes correspond to each category of interest. In a given category, each of the eleven disinfectant codes either *must* be associated with sampling locations in the category, or *may* (optionally) be associated, or *must not* be associated. (See descriptions at the bottom of Exhibit 5.4.) Note that in some of the tables, the three codes for chlorination (i.e., CLGA, CLOF and CLON) are treated as a unit, as are the three codes for chloramination (i.e., CAGC, CAOF and CAON).

UCMR 3 findings presented in Exhibit 5.4 through Exhibit 5.8 confirm that some disinfection techniques are associated with greater chlorate occurrence than others. Use of bulk hypochlorite solution or OSG hypochlorite was associated with significantly more chlorate detections (87.6 percent and 78.4 percent, respectively with bulk hypochlorite solution and OSG hypochlorite) than gaseous chlorine (16.3 percent). Chlorine dioxide is also associated with high chlorate concentrations: 90.1 percent of samples where chlorine dioxide was in use had detectable levels of chlorate. In addition, chlorate was detected in 22.3 percent of samples where no disinfectant was in use mostly among GW systems (See Appendix B.4), implying chlorate contamination in source waters.
Disinfectant Type	Gaseous chlorine only	OSG hypochlorite only	Bulk hypochlorite solution only
Disinfectant Type Code			
#Measurements	15,148	2,941	16,608
#Detections (%)	2,462 (16.3%)	2,306 (78.4%)	14,544 (87.6%)
%Detections > 210	12.2%	16.6%	27.5%
%Detections > 420	4.9%	3.9%	9.2%
%Detections > 630	2.6%	1.8%	4.1%

Exhibit 5.4: Chlorate Occurrence by Form of Chlorine

Source: UCMR 3 chlorate data available in July 2016 (USEPA, 2016e). Note: Counts include samples from both EPs and MRs. OSG = on-site generated

The disinfection codes used to categorize each sampling location are provided graphically in the table header above each column. The legend to the right indicates what code or set of codes corresponds to each cell. Fully shaded cells show codes that must be present for a sampling location to be assigned to a category, and striped cells show codes that may be present. Blank cells show codes that must not be present.

Layout Key 0						Color K	(ey
	CLGA	CAGC		OZON	OTHD		Used
	CLOF	CAOF		CLDO	NODU		May be used
	CLON	CAON		UVLV			Not used

Exhibit 5.5: Chlorate Occurrence, Chlorination versus Chloramination

Disinfectant Type	Gaseous chlorine only	Chloramination from gaseous chlorine only	OSG hypochlorite only	Chloramination from OSG hypochlorite only	Bulk hypochlorite solution only	Chloramination from bulk hypochlorite solution only
Disinfectant Type Code						
#Measurements	15,148	4,277	2,941	1,372	16,608	2,315
#Detections (%)	2,462 (16.3%)	1,435 (33.6%)	2,306 (78.4%)	1,204 (87.8%)	14,544 (87.6%)	2,111 (91.2%)
%Detections > 210	12.2%	26.6%	16.6%	52.7%	27.5%	37.2%
%Detections > 420	4.9%	9.6%	3.9%	22.2%	9.2%	12.6%
%Detections > 630	2.6%	3.6%	1.8%	11.2%	4.1%	6.2%

Source: UCMR 3 chlorate data available in July 2016 (USEPA, 2016e).

Note: Counts include samples from both EPs and MRs. OSG = on-site generated

The disinfection codes used to categorize each sampling location are provided graphically in the table header above each column. The legend to the right indicates what code or set of codes corresponds to each cell. Fully shaded cells show codes that must be present for a sampling location to be assigned to a category, and striped cells show codes that may be present. Blank cells show codes that must not be present.

Layout Key Color							Key
CLGA	CAGC		OZON	OTHD			Used
CLOF	CAOF		CLDO	NODU			May be used
CLON	CAON		UVLV				Not used

Disinfectant Type	Chlorine dioxide alone and in any disinfectant combination	Chlorine dioxide in combination with gaseous chlorine only	Chlorine dioxide in combination with OSG hypochlorite only	Chlorine dioxide in combination with bulk hypochlorite solution only
Disinfectant Type Code				
#Measurements	1,884	649	54	175
#Detections (%)	1,697 (90.1%)	580 (89.4%)	52 (96.3%)	172 (98.3%)
%Detections > 210	50.5%	38.4%	84.6%	87.2%
%Detections > 420	21.0%	12.6%	44.2%	60.5%
%Detections > 630	8.8%	4.0%	25.0%	23.3%

Exhibit 5.6: Chlorate Occurrence when Chlorine Dioxide is in Use

Source: UCMR 3 chlorate data available in July 2016 (USEPA, 2016e). Note: Counts include samples from both EPs and MRs. OSG = on-site generated

The disinfection codes used to categorize each sampling location are provided graphically in the table header above each column. The legend to the right indicates what code or set of codes corresponds to each cell. Fully shaded cells show codes that must be present for a sampling location to be assigned to a category, and striped cells show codes that may be present. Blank cells show codes that must not be present.

Layout K	еу			Color	Key
CLGA	CAGC	OZON	OTHD		Us
CLOF	CAOF	CLDO	NODU		Ма
CLON	CAON	UVLV			No

sed ay be used ot used

Disinfectant Type	Ozonation alone and in any disinfectant combination	Ozonation in combination with gaseous chlorine only	Ozonation in combination with OSG hypochlorite only	Ozonation in combination with bulk hypochlorite solution only
Disinfectant Type Code				
#Measurements	1,767	210	35	192
#Detections (%)	1,295 (73.3%)	26 (12.4%)	35 (100%)	187 (97.4%)
%Detections > 210	25.7%	11.5%	2.9%	35.8%
%Detections > 420	9.0%	7.7%	0.0%	5.9%
%Detections > 630	4.5%	7.7%	0.0%	0.0%

Exhibit 5.7: Chlorate Occurrence when Ozone is in Use

Source: UCMR 3 chlorate data available in July 2016 (USEPA, 2016e). Note: Counts include samples from both EPs and MRs. OSG = on-site generated

The disinfection codes used to categorize each sampling location are provided graphically in the table header above each column. The legend to the right indicates what code or set of codes corresponds to each cell. Fully shaded cells show codes that must be present for a sampling location to be assigned to a category, and striped cells show codes that must be present. Blank cells show codes that may not be present.

Layout K	еу				Co
CLGA	CAGC	OZON	OTHD		
CLOF	CAOF	CLDO	NODU		
CLON	CAON	UVLV		-	

Color Key Used May be used

Exhibit 5.8: Chlorate Occurrence when Other or No Disinfectants are in Use

Disinfectant Type	UV light alone and in any disinfectant combination	UV light in combination with gaseous chlorine only	UV light in combination with OSG hypochlorite only	UV light in combination with bulk hypochlorite solution only	"Other disinfectant," alone and in any disinfectant combination	No disinfectant used (at least one NODU code, and no other codes)
Disinfectant Type Code						
#Measurements	1,002	97	18	180	571	2,300
#Detections (%)	777 (77.5%)	16 (16.5%)	15 (83.3%)	175 (97.2%)	336 (58.8%)	512 (22.3%)
%Detections > 210	21.4%	12.5%	20.0%	29.7%	17.6%	8.8%
%Detections > 420	4.5%	6.3%	0.0%	5.7%	6.3%	2.3%
%Detections > 630	2.3%	0.0%	0.0%	3.4%	3.3%	1.6%

Source: UCMR 3 chlorate data available in July 2016 (USEPA, 2016e).

Note: Counts include samples from both EPs and MRs. OSG = on-site generated

The disinfection codes used to categorize each sampling location are provided graphically in the table header above each column. The legend to the right indicates what code or set of codes corresponds to each cell. Fully shaded cells show codes that must be present for a sampling location to be assigned to a category, and striped cells show codes that may be present. Blank cells show codes that must not be present.

Layout K	еу	Color k					Key
CLGA	CAGC		OZON	OTHD			Used
CLOF	CAOF		CLDO	NODU			May be used
CLON	CAON		UVLV				Not used

Since hypochlorination and chlorine dioxide are the two disinfection techniques most commonly associated with chlorate formation, only systems using those techniques were required to gather chlorate data under the DBP ICR. (For more information on the DBP ICR, refer to Appendix A.) The more recent and more comprehensive UCMR 3 survey, however, shows that chlorate is also present in other types of systems. As shown above, chlorate concentrations exceed the HRL in finished water at 12.2 percent of gaseous chlorine systems (Exhibit 5.4) and in 8.8 percent of systems using no disinfectant at all (Exhibit 5.8).

One possible explanation for the finding of chlorate occurrence with no disinfectant use is that chlorate may be present in source water. Bolyard et al. (1992, 1993) found that in a handful of cases, gas chlorinating systems had detectable levels of chlorate in both source and finished water. Investigating further, Bolyard et al. (1993) surveyed a number of source waters and found that chlorate was present at detectable levels at 7 out of 22 stream sites and 3 out of 8 ground waters. (No chlorate was detected in nine reservoirs or in three mixed surface and ground water sources.) Concentrations ranged from the reporting level (10 μ g/L) to 81 μ g/L.

Data on chlorate occurrence in ambient water could corroborate these findings. As indicated at the beginning of Chapter 5, data on chlorate occurrence in ambient water are extremely scarce. If chlorate is indeed present in significant quantities in source water, possible sources include agricultural application of sodium chlorate, industrial effluent and treated wastewater (see Section 2.2). Gorzalski and Spiesman (2015) proposed that de facto waste water reuse could be responsible for at least some of the chlorate contamination observed in systems that monitored under UCMR 3 and were chlorinating with gaseous chlorine. To test their theory, they examined a cluster of systems taking water from the Tennessee River using gaseous chlorine that had high chlorate levels. They compared the chlorate levels of systems using gaseous chlorine on the Tennessee River to other nearby systems also using gaseous chlorine, but drawing from surface water sources other than the Tennessee River. They found that 11 of 23 samples from the Tennessee River were non-detect. This led the authors to conclude that the Tennessee River likely had elevated concentrations of chlorate.

The DBP ICR database includes influent values for chlorate which presumably represent source water concentrations. This includes a total of 749 samples at 75 systems. Of the 749 influent chlorate results, 80 were above the minimum reporting level of 20 μ g/L. The average among detected concentrations was 110 μ g/L.² The median, 90th percentile and 99th percentile of influent reported positive chlorate results were equal to 37 μ g/L, 120 μ g/L and 1,442 μ g/L, respectively. These results provide further confirmation that chlorate can be present in some source waters.

Observing the wide variability in chlorate concentrations at various points in the distribution system in gas chlorinating and other systems (see Section 5.6), Gorzalski and Spiesman (2015) proposed that there may be wide temporal variability of chlorate concentrations in source water.

² Within the DBP ICR database, all the chlorate samples marked as "influent" had a sequence number of 0, indicating that the samples were truly source water samples.

Limited data gathered by Bolyard et al. (1993) (repeated samples at a single surface water site over the course of 450 days) do show considerable variation, repeatedly dipping below the reporting level (10 μ g/L) and then back up to levels in excess of 20 μ g/L or 40 μ g/L.

5.5 Occurrence of Chlorate by System Size

Exhibit 5.9 summarizes UCMR 3 results for all system sizes in the two disinfection categories most associated with chlorite formation: chlorine dioxide and hypochlorite. For comparison, a third column is included that summarizes results for all other UCMR 3 systems (those using neither chlorine dioxide nor hypochlorite). As the exhibit shows, very large systems have the lowest rates of HRL, 2xHRL and 3xHRL exceedance in all three categories. In the hypochlorite category in particular, there is a notable trend toward higher rates of exceedance at the smallest systems.

There are several factors that could explain higher rates of chlorate occurrence at smaller systems than at larger systems in the chlorine dioxide and hypochlorite categories. First, if smaller systems use chlorine dioxide, there is a risk that sub-optimal operation of chlorine dioxide generators by staff lacking specialized expertise could generate excessive chlorate. Second, if smaller systems use hypochlorite, lower flow rates and longer storage times could lead to higher concentrations of chlorate than observed in larger systems (since there are minimum sizes in which hypochlorite can be purchased). Third, smaller systems might also use more concentrated stock solutions due to relative lack of knowledge or personnel; i.e., to handle frequent dilutions of hypochlorite which could also lead to increased formation of chlorate. Fourth, many states require a minimum supply of chemicals be kept on hand, usually a 30-day supply (e.g., Great Lakes Upper Mississippi River Board of State Public Health and Environmental Managers, 1997). This may lead to extended storage times for hypochlorite solutions and higher chlorate concentrations. (See Chapter 6 below for more details.)

System Size	Measurements	Chlorine Dioxide: Number of Samples (% of Total)	Hypochlorite: Number of Samples (% of Total)	All Other Disinfectant Types: Number of Samples (% of Total)
Small Systems	Total Number of Samples	182	2,011	3,782
Small Systems	Detections > 210 µg/L	86 (47.3%)	655 (32.6%)	315 (8.3%)
Small Systems	Detections > 420 µg/L	35 (19.2%)	303 (15.1%)	120 (3.2%)
Small Systems	Detections > 630 µg/L	13 (7.1%)	153 (7.6%)	64 (1.7%)
Large Systems	Total Number of Samples	1,255	18,018	26,743
Large Systems	Detections > 210 µg/L	608 (48.4%)	4,659 (25.9%)	1,924 (7.2%)
Large Systems	Detections > 420 µg/L	270 (21.5%)	1,601 (8.9%)	680 (2.5%)
Large Systems	Detections > 630 µg/L	111 (8.8%)	737 (4.1%)	283 (1.1%)
Very Large Systems	Total Number of Samples	447	6,478	3,912
Very Large Systems	Detections > 210 µg/L	163 (36.5%)	1,472 (22.7%)	182 (4.7%)
Very Large Systems	Detections > 420 µg/L	51 (11.4%)	453 (7.0%)	67 (1.7%)
Very Large Systems	Detections > 630 µg/L	25 (5.6%)	192 (3.0%)	31 (0.8%)

Exhibit 5.9: UCMR 3 Chlorate Occurrence at Systems Using Chlorine Dioxide and Hypochlorination, by System Size

Source: UCMR 3 chlorate data available in July 2016 (USEPA, 2016e). Note: Counts include samples from both EPs and MRs.

Note: UCMR 3 monitoring was required at a representative sample of small systems (serving <10,000 people) and at all large (serving 10,001 to 100,000 people) and very large systems (serving >100,000 people) systems in the nation.

The disinfection codes used to categorize each sampling location are provided graphically in the table header above each column. The legend to the right indicates what code or set of codes corresponds to each cell. Fully shaded cells show codes that must be present for a sampling location to be assigned to a category, and striped cells show codes that may be present. Blank cells show codes that must not be present.

Layout Key Col						Color I	Key		
CLGA	CAGC		OZON	OTHD			Used		
CLOF	CAOF		CLDO	NODU			May be used		
CLON	CAON		UVLV				Not used		

5.6 Variation of Occurrence from EPs to MRs

As noted above, UCMR 3 monitoring is conducted at two sampling locations for chlorate (i.e., EP and MR locations). EPA investigated variations in occurrence to see whether concentrations rose or fell in the distribution system. Paired EP and MR concentrations were studied. In most cases only one sample was taken at each EP or MR on a particular day; if there were multiple values for a given EP or MR location they were averaged. Non-detections were assigned a value of zero.

Exhibit 5.10 is a scatterplot of paired EP and MR chlorate concentrations (restricted to measurements $\leq 500 \ \mu g/L$ for a better resolution of the graph). This plot shows a substantial variability between the chlorate concentrations at EP and MR locations among systems.

Exhibit 5.10: Distribution of Paired MR and EP Locational Average Chlorate Concentrations at All UCMR 3 Sampling Locations



Note: Based on UCMR 3 chlorate data available as of July 2016. Non-detections are assigned a value of zero. Paired non-detections are excluded from the analysis. The blue diagonal line is not a regression line; it is a line that represents all points with equal chlorate concentrations at the MR and the EP.

The scatterplot of EP and MR chlorate concentrations in sampling locations where chlorine dioxide was reported to be in use (Exhibit 5.11) shows that much of the paired chlorate concentrations lie above the blue EP = MR chlorate concentration line (i.e., they have an MR chlorate concentration greater than the EP chlorate concentration). Note the scatterplot is restricted to samples where the EP and MR chlorate concentrations were both less than or equal to 500 μ g/L for a better resolution of the graph.

Exhibit 5.11: Distribution of Paired MR and EP Locational Average Chlorate Concentrations at UCMR 3 Sampling Locations Where Chlorine Dioxide was Reported to Be in Use



Note: Based on UCMR 3 chlorate data available as of July 2016. Non-detections are assigned a value of zero. Paired non-detections are excluded from the analysis. The blue diagonal line is not a regression line; it is a line that represents all points with equal chlorate concentrations at the MR and the EP.

A scatterplot of EP and MR chlorate concentrations less than or equal to $500 \mu g/L$ for the hypochlorite category is shown in Exhibit 5.12. Like the other scatterplots above, it shows considerable variability in the chlorate levels by sample location among systems (many MR locations with higher or lower concentrations than corresponding EP locations).

Exhibit 5.12: Distribution of Paired MR and EP Locational Average Chlorate Concentrations at UCMR 3 Sampling Locations Where Hypochlorination was Reported to Be in Use



Note: Based on UCMR 3 chlorate data available as of July 2016. Non-detections are assigned a value of zero. Paired non-detections are excluded from the analysis. The blue diagonal line is not a regression line; it is line that represents all points with equal chlorate concentrations at the MR and the EP.

Possible explanations for increasing chlorate concentrations in the distribution system might include use of hypochlorite booster disinfection in the distribution system, or continuous formation of chlorate in the presence of chlorite and free chlorine residual throughout the distribution system (see Chapter 6 of this document for more discussion). Among systems with multiple entry points, mixing waters with different chlorate levels can result in lower or higher chlorate levels in the mixed water in the distribution system. Another possible mechanism for lower chlorate levels in the distribution system could be microbial degradation. Chlorate reducing bacteria are widely distributed in the natural environment (Logan, 1998); it is not known whether or to what extent they may inhabit pipe biofilms.

5.7 Comparing UCMR 3 and DBP ICR Data for Occurrence

The DBP ICR (USEPA, 1996; 61 FR 24353) required all PWSs serving at least 100,000 people to monitor and collect data on DBPs over an 18-month period from July 1997 to December 1998; a total of 296 water systems reported data. (For more details on DBP ICR, including additional occurrence analyses, see Appendix A.)

EPA performed a comparison of the DBP ICR (1998 results) to those from UCMR 3. Since the DBP ICR was limited to the nation's largest water systems (as a census of systems serving over 100,000 customers), the common systems included in the analysis conducted here are all very large systems. Only systems using chlorine dioxide or hypochlorite were included in the analysis. System identification numbers (PWSIDs) were used to link the databases. A total of 199 systems were found to have participated and reported disinfection data in both surveys. In the DBP ICR, 262 individual surface water plants reported data from these 199 systems. These results were compared with data from the 342 EP locations and 238 MR location associated with surface water source codes at the 199 systems in the UCMR 3 data set (as of July 2016). Surface water facilities were the focus of the analysis, because they were more likely to have greater chlorate occurrence than ground water facilities.

Of the 199 common systems, 47 reported chlorate data in both surveys. Exhibit 5.13 displays the results of a comparison of chlorate findings from the two surveys for common systems using chlorine dioxide or hypochlorite. The data collected under UCMR 3 between 2013 and 2016 show approximately twice the percentage of the samples with chlorate concentrations greater than the HRL compared to the samples based on the data from the 1998 DBP ICR among common systems. At the 2xHRL threshold, the higher percentage from the UCMR 3 survey is even more pronounced.

There could be a number of explanations for why chlorate occurrence has increased in the time since the DBP ICR with systems using the same disinfectant type. These may include changes in disinfectant dose, longer solution storage times or changes in disinfection practices such as methods of generating chlorine dioxide, methods for lowering chlorite, or shifts to hypochlorite over chlorine gas as a secondary disinfectant with chlorine dioxide being used as a primary disinfectant. When comparing the results of the two programs, it should be recognized that they were conducted nearly two decades apart, and that sampling schedules also differed. In the DBP ICR, systems that used chlorine dioxide were required to monitor for chlorate monthly, while those using bulk hypochlorite solution monitored quarterly for chlorate and those using other disinfectants did not monitor at all. Under UCMR 3, monitoring was conducted on a quarterly basis at surface water sampling locations, and twice per year at ground water sampling locations. Certain changes in disinfection practices over time, described in the following paragraphs, may help explain the higher rates of chlorate occurrence observed at common systems in the UCMR 3 survey compared with the DBP ICR survey.

Exhibit 5.13: DBP ICR and UCMR 3 Comparison – Chlorate Occurrence in Common Systems Using Chlorine Dioxide and Hypochlorite

Among 47 Common Systems	Measurements	Chlorine Dioxide: Number of Samples ¹	Chlorine Dioxide: Percent of Total	Hypochlorite: Number of Samples ²	Hypochlorite: Percent of Total
DBP ICR	Total Number of Samples	581		114	
DBP ICR	Detections > 210 µg/L	112	19.3%	14	12.3%
DBP ICR	Detections > 420 μg/L	13	2.2%	2	1.8%
DBP ICR	Detections > 630 μg/L	1	0.2%	1	0.9%
UCMR 3	Total Number of Samples	168		203	
UCMR 3	Detections > 210 µg/L	67	39.9%	55	27.1%
UCMR 3	Detections > 420 μg/L	20	11.9%	13	6.4%
UCMR 3	Detections > 630 µg/L	8	4.8%	2	1.0%

Notes: For DBP ICR counts, only used chlorate data collected between 1/1998 and 12/1998 (i.e., periods 7 through 18) and with the following "event codes" (representing distribution system samples): AVG, AVG1, AVG2, FINISH and MAX. For UCMR 3 counts, used chlorate data collected between 1/2013 and 5/2016.

1. Chlorine dioxide counts were identified as follows: in DBP ICR, all records with M_Source_Cat = "SW" and disinfectant type = "CLX"; in UCMR 3, all records with FacilityWaterType = "SW" and disinfectant type = "CLDO" (with or without other disinfectants).

2. Hypochlorite counts were identified as follows: in DBP ICR, all records with M_Source_Cat = "SW" and disinfectant type = "CL2"; in UCMR 3, all records with FacilityWaterType = "SW" and disinfectant type = "CAOF" or "CLOF" (without other disinfectants).

6 Formation in Drinking Water

As shown and discussed in Chapter 5, the majority of chlorate detections take place among disinfecting systems, suggesting that disinfection practices are the most common source of chlorate in drinking water; occurrence of chlorate (as a DBP) is a function of disinfectant types used. This chapter discusses possible pathways by which chlorate contamination can occur for different disinfectant types. While this chapter provides supplemental information in the context of national chlorate occurrence (as discussed in Chapter 5 of this document), it offers a scientific basis for potential control strategies, which are discussed in Chapter 7 of this document. This chapter is divided into the following sections:

- Chlorine dioxide,
- Bulk hypochlorite solution,
- On-site generated (OSG) hypochlorite,
- Ozone,
- Gaseous chlorine along with other disinfectant types.

6.1 Chlorine Dioxide

As described in the Agency's Alternative Disinfectants and Oxidants Guidance Manual (USEPA, 1999), chlorine dioxide has been used as a pre-oxidant and as an alternative to chlorine as a disinfectant in drinking water treatment. Because of its incompressible, volatile nature and explosive characteristics, chlorine dioxide cannot be shipped or stored in large quantities and is generated *in situ* for drinking water treatment (USEPA, 1999; Bergmann and Koparal, 2005; Gates et al., 2009). While use of chlorine dioxide has been effective at preventing or reducing the formation of chlorination DBPs (including trihalomethanes and haloacetic acids) and simultaneously achieving inactivation of pathogens, formation of chlorate (along with chlorite) is a well-established unintended consequence. As shown by the UCMR 3 data presented in Section 5.4, systems using chlorine dioxide alone or in combination with other disinfectants show a higher frequency of occurrence of chlorate (particularly at higher concentrations) in the finished water than systems using other forms of disinfection (see, for example, Exhibit 5.5 and Exhibit 5.8). Similar findings on the occurrence of chlorate associated with chlorine dioxide usage are also provided by the Disinfection Byproducts Information Collection Rule (DBP ICR) (see Appendix A).

There are several mechanisms that result in the formation/occurrence of chlorate in drinking water when chlorine dioxide is used. These are discussed below:

Chlorate Occurrence/Formation during Chlorine Dioxide Generation:

Gates et al. (2009) provide a comprehensive overview of generation technologies for chlorine dioxide. There are several generation methods available. Each of these involves using sodium chlorite or sodium chlorate along with other reactants such as hypochlorite, chlorine gas or acid.

During chlorine dioxide generation with any of these methods, chlorate occurrence/formation can arise from impurities in the chemicals used and/or improper operational conditions (including not using a precise chemical dose or ratio). For instance, with the generation method based on the reaction between chlorite solution and chlorine gas, the intermediate complex of Cl₂O₂ can decay to chlorate at low pH; chlorate may also result from the presence of excess hypochlorous acid (at low pH) in the mixture (Gates, 2009).

Chlorate Occurrence/Formation from Decomposition of Chlorine Dioxide:

Richardson et al. (2009) provide a comprehensive review of chlorine dioxide chemistry. Under neutral pH conditions, chlorine dioxide solution is stable. However, in strongly acidic or basic conditions (i.e., pH < 2 or > 11), chlorine dioxide can disproportionate to chlorate. Also, chlorine dioxide may undergo photodecomposition to chlorate (Bolyard et al., 1993; Gallagher et al., 1994; Bergmann and Koparal, 2005) or be present as an impurity in the chlorine dioxide (USEPA, 2006a; Gates et al., 2009). In addition, Liu et al. (2013) found that metal oxide particles CuO, Cu₂O and NiO catalyzed the disproportionation of chlorine dioxide into chlorate and chlorite, while α -FeOOH had minimal effect. Gordon et al. (1995), however, found that despite earlier research indicating transition metal catalysis of decomposition above pH 9, no accelerated chlorate formation occurred in the presence of metals such as Fe²⁺, Ni²⁺, Cu²⁺ and Mn²⁺.

Chlorate Occurrence/Formation from Conversion of Chlorine Dioxide or Chlorite:

A literature review conducted by Richardson et al. (2009) indicates that dilute solutions of chlorine dioxide are stable under low- or zero-oxidant-demand conditions, but when chlorine dioxide is in contact with organic or inorganic matter, chlorine dioxide rapidly degrades to chlorate along with chlorite and chloride. Overall, chlorate levels can be up to 20 percent of the original chlorine dioxide dose and chlorite levels can vary between 30 percent and 70 percent, depending on conditions under which chlorine dioxide is applied during water treatment. Chlorate levels can also be elevated from the oxidation of chlorite in the presence of free chlorine, as observed in a finished water storage tank in a full-scale treatment plant in Barcelona, Spain (Conio et al., 2009), and in distribution systems (Gallagher et al., 1994). In addition, adding sulfur dioxide and the sulfite ion to reduce the concentrations of chlorine dioxide and chlorite residuals when using chlorine dioxide (Gordon et al., 1990) can result in the formation of chlorate (Griese et al., 1991). Sulfur dioxide and/or sulfite (as S(IV)) are thought to accelerate the disproportionation of chlorine dioxide to produce chlorate, although other reactions are prevalent and result in the formation of chlorite (Griese et al., 1991).

Korn et al. (2002) developed empirical equations to model the disappearance of chlorine dioxide and the formation of chlorite and chlorate. The models were validated against measurements of these species from water systems. The authors indicate that, on average, 68 percent by mass of chlorine dioxide consumed becomes chlorite, while 9 percent by mass of chlorine dioxide consumed becomes chlorate. The most important parameters cited for the formation of chlorite and chlorate were chlorine dioxide concentration, non-purgeable organic carbon concentration and ultraviolet (UV) absorbance at 254 nm of the aqueous solution. Such model predictions could underestimate chlorate occurrence in the distribution systems if chlorine dioxide is used in treatment plants as an oxidant/disinfectant and free chlorine is used in distribution systems as a disinfectant residual, primarily due to the reaction between chlorite and free chlorine as discussed earlier. By studying byproduct residuals in water treated by chlorine dioxide generated with sodium chlorite and free chlorine, Gallagher et al. (1994) estimated that between 60 and 85 percent of chlorate occurrence in the distribution system was attributable to the reaction between free chlorine residual and chlorite, and between 15 and 40 percent was associated with the generator.

6.2 Bulk Hypochlorite Solution

As discussed earlier, commercial hypochlorite solutions (or bulk hypochlorite solution) have become a more-commonly used form of chlorine for water treatment. One of the unintended consequences associated with use of hypochlorite solutions is occurrence/formation of chlorate. Nieminski et al. (1993) surveyed six water treatment plants using hypochlorite and found chlorate concentrations up to 700 μ g/L in finished water. They also observed no detection of chlorate when gaseous chlorine was used.

Bolyard et al. (1992) examined bulk hypochlorite solutions from 14 drinking water utilities in the United States. At a reporting limit of 10.0 μ g/L, chlorate was detected in each of the 14 hypochlorite solutions, with concentrations ranging from 180,000 to 42,000,000 μ g/L. A second set of analyses was performed on the same solutions approximately four months later using smaller dilution ratios, which allowed for quantitation in a range of high precision and for lower detection/reporting levels. Chlorate was again detected in all 14 solutions, with concentrations ranging from 190,000 to 50,000,000 μ g/L.

The same study found that the chlorate in the bulk solutions carried over into the drinking water at all 14 utilities. Concentrations in finished water ranged from 11 μ g/L to 660 μ g/L. Three samples exceeded the Health Reference Level (HRL) of 210 μ g/L, with concentrations of 320, 600 and 660 μ g/L. The two highest concentrations also exceeded twice the HRL. Chlorate was also detected in 2 (14 percent) of 14 source water samples (with concentrations of 20 μ g/L and 22 μ g/L) collected at the 14 drinking water utilities. In both cases, finished water samples had higher chlorate concentrations (Bolyard et al., 1992).

A follow-up study (Bolyard et al., 1993) presented additional details and reported the results for one additional water system using hypochlorite solution for disinfection. Chlorate was detected in the treated water at this system at a concentration of 49 μ g/L, but was not detected in the system's source water (at a reporting limit of 10.0 μ g/L). Overall, Bolyard et al. (1992, 1993) detected chlorate in 15 (100 percent) of 15 treated drinking water samples disinfected with hypochlorite solution.

For comparison, Bolyard et al. (1993) also conducted sampling at utilities that use gaseous chlorine for disinfection rather than sodium hypochlorite. Chlorate was detected in three (11 percent) of 28 treated drinking water samples (with concentrations ranging from 17 μ g/L to 43 μ g/L) and in 2 (13 percent) of 16 source water samples (at concentrations of 17 μ g/L and 81 μ g/L). All detected concentrations of chlorate were below the HRL. The study authors interpreted their data to indicate that use of hypochlorite solution led to chlorate formation and the use of gaseous chlorine did not.

Gordon et al. (1993) confirmed the presence of chlorate at concentrations of 330,000 μ g/L to 15,600,000 μ g/L in hypochlorite feedstocks used at 16 utilities. (Hypochlorite concentrations in the feedstocks ranged from 1,680,000 μ g/L to 95,900,000 μ g/L.) Chlorate was found in finished drinking water samples from 16 (100 percent) of 16 utilities at concentrations ranging from 30 μ g/L to 300 μ g/L. Reporting levels were not identified in this study; for perspective, the minimum detected concentration (30 μ g/L) is three times that of the reporting limit in the Bolyard et al. (1992, 1993) studies. One of the 16 utilities had chlorate concentrations that exceeded the HRL (and another had a concentration equal to the HRL); none of the sample results exceeded twice the HRL. In a follow up study, Gordon et al. (1995) indicated that chlorate concentrations in finished water were higher at facilities that used hypochlorite solutions for disinfection (mean chlorate concentration of 0.49 mg/L) than at facilities that used chlorine dioxide (mean chlorate concentrations of 0.25-0.29 mg/L).

Stanford et al. (2011) examined hypochlorite solutions from six utilities using either bulk hypochlorite solution or on-site hypochlorite generation. They found chlorate concentrations ranging from 760,000 to 19,000,000 μ g/L in the bulk hypochlorite solutions. Chlorate concentrations in the finished water ranged from 19 to 1,500 μ g/L. Three of the seven finished water samples had chlorate concentrations greater than the HRL. Based on the observations of bulk hypochlorite solutions they developed a kinetic model of the decomposition of hypochlorite. They found that hypochlorite initially decomposes to form chlorate and chloride. The formed chlorate can then react with another hypochlorite molecule to form perchlorate. They found the initial reaction was second order in hypochlorite concentrations were dependent on temperature and ionic strength. Their model, which was only valid for stock solutions at pH between 11 and 13, showed good agreement with the actual decomposition (Snyder et al., 2009; Stanford et al., 2011).

Gordon et al. (1993) showed that at the initial hypochlorite concentration of 11.5 percent, chlorate levels in the solution appeared relatively steady (i.e., between approximately 2 and 6 g/L) at 10 degrees C over the course of 30 days of storage. However, at higher temperatures the chlorate levels increased: e.g., to over 18 g/L over the course of 30 days at 25 degrees C. The study also demonstrated that at a given temperature, the increasing trend was less pronounced with lower initial hypochlorite concentrations. Gordon et al. (1995) and Stanford et al. (2011) confirmed that the decomposition of hypochlorite solutions during storage was a probable source of chlorate formation under the conditions of relatively high temperatures and/or initial hypochlorite concentrations. In this formation mechanism, hypochlorite disproportionates in basic solutions to chlorite and finally to chlorate (Bolyard et al., 1992; Bolyard et al., 1993). The decomposition can be accelerated by sunlight (Gallagher et al., 1994). Upon a literature review and analysis of field data, Snyder et al. (2009) and Stanford et al. (2011) identified and assessed the key factors (besides sunlight) affecting chlorate (along with perchlorate and bromate) occurrence/formation during the storage of hypochlorite solutions. These factors include the dilution rates of the solution on delivery, temperature, pH, levels of transition metal ions and storage time. Upon these reports, the American Water Works Association (AWWA, 2012) developed a web-based predictive modeling tool (available exclusively to AWWA members) that provides guidance on the expected levels of chlorate (along with perchlorate) in stored bulk hypochlorite solutions. Further discussion of these individual factors and the AWWA predictive tool is presented in Chapter 7 of this document in context of chlorate control strategies when

hypochlorite solutions are used. Overall, chlorate levels increase linearly with storage time. Compounding this problem is the concomitant decrease of available chlorine in the hypochlorite solutions as they age, which causes the need for the addition of larger volumes of hypochlorite to achieve the required residual of available chlorine, thereby introducing even more chlorate into the treated drinking water (WHO, 2005).

6.3 On-Site Generated Hypochlorite

In addition to delivery of bulk hypochlorite solution, hypochlorite can be produced on-site via the electrolysis of brine. AWWA (2015) developed a Manual of Water Supply Practices—M65 for on-site generation (OSG) of hypochlorite. In 2009, Snyder et al. estimated that 8 percent of utilities used OSG to produce hypochlorite for disinfection (Snyder et al., 2009). More recent UCMR 3 data indicated that 15 percent of UCMR 3 systems that reported disinfectant types used OSG hypochlorite. Thus, it appears that there is an increasing trend toward use of site-generated hypochlorite in lieu of chlorine gas. Snyder et al. (2009) also indicated that OSG could result in the formation of oxyhalides, including chlorate and perchlorate. As discussed in Chapter 5, the UCMR 3 confirms that elevated chlorate levels occur much more frequently when OSG hypochlorite is used, as compared to chlorine gas.

According to the M65 Manual (AWWA, 2015), commercially available OSG systems typically consist of electrolytic cells that initiate an electro-oxidation process. This process converts chloride (typically fed as a sodium chloride brine) to hypochlorite. In general, the OSG systems can be grouped into low- and high-strength systems. Low strength-generators typically generate 0.4 percent to 0.8 percent hypochlorite from electrolysis of brine. The electrolyzed brine is then fed directly into a day tank for short-term (48 hours or less) storage and/or is then pumped into the water stream for disinfection. High strength units generate chlorine gas, which is then mixed with water to produce hypochlorite at concentrations of 12 percent to 15 percent (roughly equivalent to the concentration in bulk hypochlorite solution) and can be stored or used immediately.

Stanford et al. (2013) conducted a comprehensive study for understanding oxyhalide formation during hypochlorite OSG, and Stanford and Rivera (2015) later summarized this study in Chapter 4 of the M65 Manual (AWWA, 2015). This study involved collecting chlorate occurrence data through 54 samples from 26 low-strength and 3 high-strength OSG systems. The formation of chlorate was widely variable among different individual OSGs. Of six OSG systems studied, the formation of chlorate exhibited no apparent bias based on age, size or manufacturer of the units. Measured chlorate concentrations ranged from 5 to 90 µg of chlorate per mg/L of hypochlorite generated (Stanford et al., 2013). Overall, high-strength OSGs, which could be attributable to the difference in the process used to generate the final hypochlorite solution. Chlorate generated during the electrolysis process with a low-strength OSG (with a direct application of generated hypochlorite) could be carried into the water being treated but would not move into treated water in the case of a high-strength OSG (where hypochlorite is applied by introducing generated chlorine gas into a caustic solution). However, these observations may be limited due to the small sample size.

While limited information is available from systems at full scale, a number of laboratory studies have been conducted to evaluate the formation of byproducts such as chlorate and to determine formation mechanisms and means of optimization, as discussed below. While conditions in these laboratory studies likely differ from conditions in full-scale systems, the types of reactions and the products formed in the laboratory are likely similar to those in full-scale systems.

Bergmann and Koparal (2005) indicate that chlorine dioxide is a primary byproduct of the electrolysis of chloride-containing water and that this process can also lead to the formation of chlorite and chlorate, with chlorite being predominant. However, Vacca et al. (2013) found that chlorate was the only chlorine byproduct formed when using boron-doped diamond electrodes in a brine solution containing 20 g/L of chloride. They found up to 7 g/L of chlorate were produced by a current density of 5 milliamperes per square centimeter (mA/cm²) with a residence time of 4 minutes.

Conversely, Li and Ni (2012) found that chloroform, chlorate and perchlorate were formed at various time intervals when using a boron-doped diamond electrode in a brine solution containing 10 millimolar (mM) of chloride (355 mg/L as chloride ion; converted) following the application of a current density of 20 mA/cm² over the course of 25 hours. Chloroform and chlorate were formed initially as free available chlorine production increased. A peak chlorate concentration of 1.67 mM (139 mg/L as chlorate ion, converted) was observed after 4 hours. As free available chlorine levels decreased, chlorate was oxidized to perchlorate, which was the sole target DBP remaining at 25 hours, peaking at 3.84 mM (382 mg/L as perchlorate ion, converted) (Li and Ni, 2012).

Anodic oxidation of sodium chloride solutions can result in oxidation of hypochlorite to produce chlorate. This reaction can be viewed either as the reaction of hypochlorous acid or hypochlorite with water to produce chlorate, chloride, protons, oxygen and electrons (Czarnetzki and Janssen, 1992). It has also been suggested that anodic reactions can directly oxidize chloride to chlorate (Tasaka and Tojo, 1985). Vacca et al. (2013) have also suggested that hydroxyl radical formation from hydrolysis of water at the anode may contribute to chlorate formation. Bergmann et al. (2014) report that radical-generating electrodes had a strong tendency to produce chlorate in a laboratory-scale electrochemical reactor. Yoon et al. (2013) found that using 100 mg/L of chlorate in the feed solution resulted in the production of between 1.7 and 4.8 mg/L of chlorate depending on the electrode type.

6.4 Ozone

Ozone is also used as a drinking water oxidant/disinfectant. Because ozone is highly reactive and only moderately soluble in water, it does not maintain a residual in the drinking water distribution system. As a result, EPA has suggested that when ozone is used, it is done in conjunction with a secondary chlorine-based disinfectant such as chlorine, chlorine dioxide or chloramine (USEPA, 1999).

Siddiqui (1996) indicates that when ozone is used in the presence of hypochlorous acid in equilibrium with hypochlorite ion, oxidation of hypochlorite, first to chlorite and then to chlorate, takes place via two primary mechanisms. The first mechanism involves chloroxyl and hydroxyl radicals, while the second, slower mechanism involves direct attack of ozone on

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hypochlorite and chlorite. The kinetics of the conversion of hypochlorite to chlorate are complicated by the presence of organic matter and alkalinity, which may scavenge free radicals. Siddqui (1996) further studied the effect of solution pH during ozonation and found that the formation of chlorate was reduced by more than 85 percent when the pH was reduced from 8.0 to 6.0. The generation of hydroxyl radical was observed to be reduced by 85 percent as a result of this pH adjustment.

Another study (von Gunten, 2003) confirms these two mechanisms of chlorate formation; however, the author indicates that the reaction involving hydroxyl radicals is much less important than the more rapid reaction of chlorite directly with ozone. The paper also indicates that the formation of oxychlorine species, including chlorate, only occurs during ozonation if pretreatment with chlorine or chlorine dioxide is performed. Rakness (2015) presents a full-scale case study of pre-oxidation with chlorine dioxide used to reduce bromate formation in an ozonation plant. He finds that although pre-oxidation with chlorine dioxide forms chlorite, and chlorite creates ozone demand for the post-ozone contactor, the total ozone dose is reduced. More importantly, such an operation can result in the nearly complete oxidation of chlorite to chlorate (i.e., the plant effluent chlorite concentration is below the detection limit) while substantially reducing bromate formation. In addition, the Water Research Foundation (WRF) identifies application of ozone as one option to reduce chlorite levels in its fact sheet Strategies to Control Disinfection By-Products (WRF, 2012).

6.5 Gaseous Chlorine along with Other Disinfectant Types

As discussed earlier, an application of gaseous chlorine alone as a disinfectant will generally not lead to occurrence of chlorate in treated water. However, free chlorine residuals in water can be oxidized by ozone (a stronger oxidant than chlorine) into chlorate. In addition, free chlorine itself can be an oxidant in the presence of chlorite and can oxidize chlorite to chlorate. Furthermore, a recent study with UV light by Wang et al. (2015b) shows that UV can partially convert chlorine to chlorate. They find that 2 to 17 percent of the chlorine entering the UV reactor is converted to chlorate, with UV doses of 1800 millijoules/cm² and chlorine doses varying from 2 to 10 mg/L. Similar conversion rates (5–11 percent) are also found at 13 to 20 kilojoules per square meter by Cimetiere and De Laat (2014).

7 Treatment

Building upon the discussion of chlorate occurrence in Chapter 5 and formation in Chapter 6, this chapter discusses treatment and other strategies that have been used for reducing concentrations of chlorate in drinking water. The discussion in this chapter is divided into the following three categories:

- Reduction of disinfectant demand,
- Modification of disinfection practices,
- Removal of chlorate

7.1 Reduction of Disinfectant Demand

As discussed earlier in this document, the occurrence of chlorate at elevated levels in most cases is associated with the use of disinfectants or oxidants. Chlorate levels generally increase with an increased dose of disinfectants (including with use of chlorine dioxide or hypochlorite solution). Therefore, one potential strategy for reducing the concentration of chlorate in drinking water is to reduce the doses of the disinfectants that lead to chlorate occurrence. For instance, Sorlini et al. (2014) found that pre-oxidation with hypochlorite could reduce the amount of chlorate formed by chlorine dioxide disinfection of a groundwater source. They also found the reduction in chlorate formation was achieved by using powdered activated carbon (PAC) adsorption prior to the disinfection. They were able to lower chlorate formation by 20 to 30 percent using PAC prior to addition of chlorine dioxide.

Reduction of disinfectant dose (while maintaining the disinfection credits for compliance with the microbial rules) can be accomplished by practicing better source water management to reduce disinfectant demand (source water management may include bank filtration, as discussed in the Six-Year Review 3 Technical Support Document for Disinfectants and Disinfection Byproducts Rules (D/DBPRs) (USEPA, 2016a)). Also, use of alternative oxidants for preoxidation (including permanganate and hydrogen peroxide, as described in the Agency's Alternative Disinfectants and Oxidants Guidance Manual (USEPA, 1999)) can be considered, especially for source water contaminated by inorganic reductants such as sulfide, iron and manganese. In addition, removal of organic matter during treatment (for instance, via enhanced coagulation, biofiltration or granular activated carbon (GAC)) prior to application of disinfectants is also generally helpful for reducing the dose of disinfectant needed (USEPA, 2016a). Furthermore, improving the biostability of treated water and management of distribution systems can reduce the need for additional application of disinfectants in distribution systems, thus reducing elevated levels of chlorate throughout distribution systems (Hammes et al., 2010). Overall, these potential strategies can be evaluated in the context of the water system's sitespecific conditions for their applicability, effectiveness and unintended consequences for chlorate control. For more detailed discussion, see the Six-Year Review 3 Technical Support Document for Disinfectants/Disinfection Byproducts Rules (USEPA, 2016a), Alternative Disinfectants and Oxidants Guidance Manual (USEPA, 1999), and the Simultaneous Compliance Guidance Manual for the Long Term 2 and Stage 2 DBP Rules (USEPA, 2007).

7.2 Modification of Disinfection Practices

This section is organized by the same categories as those used for discussion of chlorate formation in Chapter 6:

- Chlorine dioxide,
- Bulk hypochlorite solution,
- On-site generated (OSG) hypochlorite,
- Ozone,
- Gaseous chlorine along with other disinfectant types.

7.2.1 Chlorine Dioxide

As mentioned earlier, chlorine dioxide is usually generated on site for drinking water treatment, and chlorate can occur as a byproduct during generation of chlorine dioxide, during storage, or after application of chlorine dioxide.

Storage of chlorine dioxide as a solution is a rare practice, and this section does not cover this practice. When chlorine dioxide is generated and introduced into the treatment train as a gas, cogenerated chlorate (as an ion) will generally not be introduced into the water. However, when chlorine dioxide is generated and introduced to the treatment train in solution, excess dissolved chlorine gas in the solution could form hypochlorite and react with chlorite to form chlorate. Therefore, maintaining optimal reagent ratios is critical to minimizing chlorate formation in treated water from such a pathway (Gates et al., 2009). Developments in feedstock delivery systems (e.g., automatically monitored systems that help to maintain proper reagent ratios) have helped in the optimization of chloride dioxide generation (Gallagher et al., 1994). The following methods may help to reduce chlorate formation during chlorine dioxide generation (USEPA, 1999; Gates et al., 2009):

- Avoid very low (<3) and very high (>11) pH;
- Avoid large excess of free chlorine relative to chlorite ion and high free chlorine concentrations at low pH; and
- Avoid excess hypochlorous acid, which can oxidize chlorite to chlorate rather than to chlorine dioxide.

One strategy for chlorate control is to reduce chlorine dioxide demand prior to applying chlorine dioxide because less chlorate is generally produced with a lower chlorine dioxide dose. See the previous section for more discussion on this strategy. As discussed in Chapter 6, chlorite and chlorine dioxide can be converted to chlorate when they co-exist with ozone or free chlorine residuals in water. Thus, a second strategy to lower chlorate levels may be to minimize use of ozone or free chlorine during water treatment and in distribution systems. For instance, in situations where chlorine dioxide is a preferred primary disinfection process, systems could

consider using chloramines rather than free chlorine as a disinfectant residual. Reducing chlorite levels using thiosulfate ion or ferrous ion in lieu of ozone may also be effective in lowering chlorate.

As stated in Chapter 6, the use of sulfur dioxide or sulfite ion as a reducing agent to control chlorine dioxide and chlorite residuals in treated drinking water can result in the formation of chlorate. In contrast, the use of thiosulfate ion or ferrous ion as alternatives to sulfur dioxide/sulfite ion did not result in appreciable formation of chlorate (Griese et al., 1991). Subsequent research by Griese and co-workers indicated that the use of ferrous ion at pH 5.0–5.6 could result in increased chlorate concentrations, and this increase could be prevented by maintaining the pH at 7.0–7.5 with lime (Griese et al., 1992).

7.2.2 Bulk Hypochlorite Solution

Predictive models have been developed to determine chlorate levels during storage of hypochlorite solutions. For example, the American Water Works Association (AWWA) has developed a web-based predictive model for assessing the factors that contribute to the formation of chlorate along with perchlorate and other contaminants related to hypochlorite solutions (Snyder et al., 2009).³ The model predicts concentrations of chlorate and perchlorate in hypochlorite solutions based on user-specified, site-specific input data (or default inputs if specific data are not known). Input data include initial hypochlorite concentration; specific gravity; pH; specific conductance; initial chlorate, perchlorate and chloride levels; and storage temperatures and durations. The model output includes graphs of predicted changes in hypochlorite, chlorate and perchlorate and dissolved oxygen. With the considerations of the quality of initial hypochlorite stock solution and doses that need to be applied, this tool can help utilities determine a maximum storage time and a series of storage conditions needed to meet a targeted level of chlorate in treated water.

Overall, to minimize the decomposition of hypochlorite solutions (to chlorate) stored at drinking water facilities, the following have been recommended (Gordon et al., 1995; Stanford et al., 2011):

- Assessing the initial quality of hypochlorite stock upon receipt by at least measuring hypochlorite, chlorate concentrations and pH,
- Dilution of hypochlorite solutions immediately upon receipt,
- Maintaining hypochlorite solutions at low temperature,

³ The model is posted on the AWWA website at the following URL: <u>http://www.awwa.org/resourcestools/waterandwastewaterutilitymanagement/hypochloriteassessmentmodel.aspx</u>.

AWWA member credentials are required to access the model.

- Avoiding exposure of hypochlorite solution to sunlight,
- Measuring pH periodically, keeping the pH in the range of 11–13,
- Avoiding extended storage times for hypochlorite solutions, and
- Considering the alternative of using solid calcium hypochlorite, which decomposes much more slowly.

7.2.3 On-Site Generation of Hypochlorite

As discussed in Chapter 6, AWWA has published a comprehensive manual regarding hypochlorite OSG (AWWA, 2015). The manual summarizes the principles of disinfection; regulations and standards; the principles of electrolytic cell operations; the available OSG systems; design, installation and operational considerations; economics of OSG; and DBP formation and control. As described in Chapter 6, the manual cites Stanford et al. (2013), who explain that high-strength OSGs generally produce less chlorate on a per-milligram free chlorine concentration basis than low-strength OSGs, because chlorate generated with a low-strength OSG. Thus, high-strength OSGs may be preferred for controlling chlorate occurrence in treated water.

In laboratory studies, Yoon et al. (2013) found that the type of electrode used affected the production of chlorate. They tested platinum, iridium and ruthenium electrodes in a laboratory set-up. They found that with 100 mg/L of chloride in the feed water, platinum electrodes produced 5 mg/L of chlorine and 4.8 mg/L of chlorate, iridium electrodes produced 48 mg/L of chlorine and 2.5 mg/L chlorate, and ruthenium electrodes produced 96 mg/L of chlorine and 1.7 mg/L chlorate, respectively. As noted in Chapter 6, Vacca et al. (2013) hypothesize that the formation of chlorate may be due to reaction of chloride to form chlorine and the reaction of water to form hydroxyl radicals are in competition with each other. They suggest electrodes with higher overpotentials for hydrolysis of water, such as boron-doped diamond, to reduce chlorate formation. They found that lower current densities, shorter residence times and higher chloride concentrations led to lower chlorate production. While the reactions taking place during electrochemical disinfection are still being studied, it appears that altering electrode materials and operating parameters can help reduce chlorate formation.

7.2.4 Ozone

As discussed in Chapter 6, ozone can react with chlorine (or hypochlorous acid), chlorine dioxide, or chlorite to form chlorate. Based on this understanding of chlorate chemistry, it is important to minimize the encounter of ozone with chlorine species for chlorate control when ozone is used as a disinfectant or oxidant. For instance, if ozone is used as a primary disinfectant and chlorine is used as a secondary disinfectant, monitoring of ozone residual can be conducted prior to application of chlorine to ensure that there is essentially no or very low ozone residual. Also, thiosulfate ion or ferrous ion in lieu of ozone can be used for reducing chlorite levels (Griese et al., 1991, 1992).

7.2.5 Gaseous Chlorine along with Other Disinfectant Types

As discussed in Chapter 6, an application of gaseous chlorine alone as a disinfectant will generally not lead to occurrence of chlorate in treated water. However, chlorine can react with chlorite/chlorine dioxide or ozone to produce chlorate. In addition, ultraviolet light (UV) can convert the chlorine residual to chlorate. Therefore, the chemistry of chlorate formation suggests that if chlorine is being applied prior to the application of chlorine dioxide or ozone in the treatment train (for instance, as a pre-oxidant to reduce formation of bromate from ozone in the presence of relatively high levels of bromide), water systems may consider reducing or eliminating chlorine residuals before applying chlorine dioxide or ozone. If chlorine is being applied after the application of chlorine dioxide or ozone (for instance, where chlorine dioxide or ozone is the primary disinfectant and chlorine is the secondary disinfectant), water systems may consider reducing chlorite levels (and chlorine dioxide residual levels) or ozone residual levels before chlorine is applied. In addition, water systems could consider improving distribution system management practices to reduce chlorine doses (while still maintaining adequate chlorine residual levels for disinfection) and reduce the elevated levels of chlorate that result from the continuous reaction between chlorite and chlorine throughout distribution systems. In the case of UV, it may be beneficial to minimize chlorine residual levels in the influent to an UV unit.

7.2.6 Removal of Chlorate

A few studies have examined methods for removal of chlorate, although none appear to have demonstrated effectiveness at full scale at a water treatment system (Gonce and Voudrias, 1994; Westerhoff and Johnson, 2001; Westerhoff, 2003; Srinivasan and Sorial, 2009; Kishimoto et al., 2015; Sivasubramanian, 2015). An early demonstration with a GAC column from Gonce and Voudrias (1994) indicates that all influent chlorite was reduced to chloride by GAC, and chlorate was not reduced but was only physically and reversibly sorbed by GAC. A much higher sorption capacity of chlorate was observed at pH 5 (4.9 mg/g) than pH 7 (0.5 mg/G).

Westerhoff and Johnson (2001) describe a study of a system designed to treat contaminated groundwater with zero valent iron. They reported the complete reduction of chlorate by zero valent iron, but the reaction was slow, with a half-life of over 200 minutes, even at 28°C. A zero valent iron reactor might remove 30 percent of the chlorate with a 20-minute contact time. A further bench-scale study conducted by Westerhoff (2003) suggests that higher solid (Fe⁰)-to-liquid ratios increase chlorate reduction, and water system operators scaling up must consider the solid-liquid ratios. Srinivasan and Sorial (2009) found that the chlorate reduction obtained with zero-valent iron filings was better than that obtained with electrochemical reduction, even in the presence of catalysts and with thin film-coated electrodes.

Sivasubramanian (2015) evaluated the effectiveness of combinations of four reducing agents (sulfite, dithionite, sulfide and ferrous iron) and three UV light sources (UV-L, UV-M and UV-B) for chlorate removal. This author found that dithionite irradiated by broad-band UV-B lamp, which has output between 280 nm and 320 nm with peak energy at 312 nm, showed the highest chlorate removal. Kishimoto et al. (2015) demonstrated that vacuum ultraviolet photolysis at 172 nm was more effective for chlorate removal than conventional UV photolysis at 254 nm. However, vacuum ultraviolet photolysis may not be feasible in water with a high concentration of nitrate due to a strong inhibitory effect from nitrate. The literature reviewed by Richardson et

al. (2009) show that ferrous iron can be effective for removing chlorite by reducing it to chloride, but not effective for removing chlorate. Overall, it appears that there is not a practical process yet for removing or reducing chlorate in drinking water supplies. Therefore, the prevention of chlorate contamination or formation is the most practical method for lowering chlorate exposure.

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Appendix A Supplemental Data Sources

Occurrence data for chlorate are available from several sources in addition to UCMR 3. Those sources include the Disinfection Byproducts Information Collection Rule (DBP ICR), the 2006 Community Water System Survey (CWSS) and a dataset compiled by the Environmental Working Group (EWG). These data are described below.

A.1 Disinfection Byproducts Information Collection Rule (DBP ICR), 1997-1998

The DBP ICR (USEPA, 1996; 61 FR 24353) required all public water systems (PWSs) serving at least 100,000 people ("very large systems") to monitor and collect data on DBPs over an 18-month period from July 1997 to December 1998. The DBP data were reported from 296 water systems, most serving a population of over 100,000. (In the end, one participating ground water system and two surface water systems reported serving populations less than 100,000.) Details on the data collection process for the DBP ICR, along with an independent analysis of the data, can be found in a report sponsored by the Microbial/Disinfection Products Council (MDPC) (McGuire et al., 2002). Some relevant aspects of the sampling protocol are described in Chapter 2 of the *Regulatory Determinations 3 Support Document* (USEPA, 2015b). The dataset used for analysis here was generated with the Aux1 database (version 5.0) of information collected under the DBP ICR.

Of the 296 water systems participating in the survey, 82 reported chlorate results. According to the survey design, only those that used chlorine dioxide or hypochlorite solutions for disinfection were required to monitor for chlorate (USEPA, 1996; 61 FR 24353). Hypochlorite use triggered quarterly sampling for chlorate at the entry point to the distribution system (EP). Chlorine dioxide use triggered monthly sampling for chlorate at the EP and at three points within the distribution system: near the first customer, in the middle of the distribution system, and at a point representative of maximum residence time in the distribution system (MR). (In practice, it appears that the EP was generally also counted as the sampling point "near the first customer.") Systems were not required to indicate whether monitoring was triggered by use of chlorine dioxide or sodium hypochlorite, but a review of sampling locations suggests that monitoring at 31 plants, belonging to 22 systems, may have been triggered by chlorine dioxide use. Hypochlorite use may have triggered monitoring at the other plants and systems. However, it is possible that both chlorine dioxide and hypochlorite may have been in use at some plants, and it cannot be ruled out that some chlorate samples were collected and reported from systems that used neither disinfectant and misunderstood the reporting requirements.

An inventory of chlorate results by system is presented in Exhibit A.1. Results are broken out by source water type and primary disinfectant type. Source water type and primary disinfectant type were determined based on information reported in the DBP ICR database. Bins for results where chlorine or chloramines were the primary disinfectant are labeled "sodium hypochlorite," on the assumption that sodium hypochlorite was used to generate the primary disinfectant in most or all of those cases. Note, however, that there may have been exceptions. Some chlorinating systems, for example, gathered chlorate results on a schedule and at sampling locations characteristic of monitoring triggered by chlorine dioxide use.
In cases where the primary disinfectant field in the DBP ICR database was blank, results were binned based on the presumed trigger for chlorate monitoring. Those with sampling locations characteristic of chlorine dioxide monitoring were binned with chlorine dioxide systems, and the rest were binned with chlorinating/chloraminating ("sodium hypochlorite") systems. While sampling locations provide a reasonable basis for inferring that chlorine dioxide or sodium hypochlorite was used at these systems, the assumption that chlorine dioxide or hypochlorite-generated chlorination/chloramination was the *primary disinfectant* used at these systems is an assumption made for convenience in this report.

Ozone was listed as the primary disinfectant at nine systems in the database. Based on sampling locations, one ozone system appears to have had chlorate monitoring triggered by chlorine dioxide use and the others do not. Since chlorine dioxide is normally used in the treatment plant and not the distribution system, an assumption was made that at the first system both chlorine dioxide and ozone should be considered primary disinfectants. In the remaining eight ozone systems, which all used chlorine and/or chloramines in the distribution system, an assumption was made that monitoring was triggered by use of sodium hypochlorite to generate chlorine for secondary disinfection.

All ground water systems in the database were included in the "hypochlorite" bin.

It will be seen in Exhibit A.1 that some systems are listed in more than one category. This happened when systems had multiple plants with different primary disinfectants. It also happened when a plant changed disinfectant type during the sampling period. In such cases, samples are distributed appropriately among the two categories. For example, if a system had a single plant that used chlorine dioxide for 12 months and hypochlorite for 6 months then it is categorized as both a chlorine dioxide system with 12 months' worth of samples and a hypochlorite system with 6 months' worth of samples. Because of double-counting, the values in the "Systems" and "Population Served" columns do not add up to the totals at the bottom of the table.

Source Water Type	Primary Disinfectant Type	Total Number of Samples	Total Number of Systems	Total Population Served by Systems
SW	Hypochlorite	420	49	30,972,523
SW	Chlorine Dioxide and Ozone	50	1	223,411
SW	Chlorine Dioxide	1,063	21	5,947,815
SW	Ozone	53	8	5,156,001
GW	Hypochlorite	133	17	6,146,635
Total		1,719	82	41,584,457

Note: Systems that had multiple plants with different primary disinfectants, or that had changes in disinfection practices, are counted in multiple rows. Therefore, the numbers in the "Systems" and "Population Served" columns do not add up to the values in the "total" row.

A.1.1 Summary Analysis

An analysis of chlorate occurrence data from the DBP ICR is presented in Exhibit A.2 through Exhibit A.6. With a minimum reporting level (MRL) of 20 μ g/L, chlorate was detected in 1,490 (86.7 percent) of 1,719 samples collected at the 82 systems. Of the 1,719 samples, 332 (19.3 percent) reported concentrations greater than the Health Reference Level (HRL) (210 μ g/L) and 101 (5.9 percent) reported concentrations greater than twice the HRL (420 μ g/L). Thirty-four systems (41.5 percent) reported concentrations of at least one sample exceeding the HRL, and 11 systems (13.4 percent) reported concentrations of at least one sample exceeding twice the HRL. The maximum detected concentration was 2,234 μ g/L, and the median detected concentration was 120 μ g/L. The mean concentration among samples with detections (not shown in the tables) was 172 μ g/L.

Exhibit A.4 shows that only five systems had no detections at all; these were all surface water systems disinfecting with hypochlorite. Hypochlorite systems, both surface water and ground water, also had the lowest rates of HRL and 2xHRL exceedance at the system level (Exhibit A.5 and Exhibit A.6). On the other hand, surface water and ground water systems using hypochlorite had the highest chlorate concentrations reported in the DBP ICR database (Exhibit A.2). Although ozone systems and chlorine dioxide systems had higher rates of HRL and 2xHRL exceedance than surface water hypochlorite systems at the system level (Exhibit A.5 and Exhibit A.6), the reverse is true at the sample level (Exhibit A.3). Very high rates of occurrence in the "chlorine dioxide plus ozone" category (e.g., in Exhibit A.3) may reflect sampling at a single system.

Exhibit A.2: Chlorate DBP ICR Occurrence Data from Systems Required to Monitor – Summary of Detected Concentrations

Source Water Type	Primary Disinfectant Type	Minimum of Detected Concentrations (µg/L)	Median of Detected Concentrations (µg/L)	90 th Percentile of Detected Concentrations (µg/L)	99 th Percentile of Detected Concentrations (µg/L)	Maximum of Detected Concentrations (µg/L)
SW	Hypochlorite	20	99	484	1,787	2,234
SW	Chlorine Dioxide and Ozone	100	620	846	995	1,000
SW	Chlorine Dioxide	20	129	260	511	880
SW	Ozone	20	114	284	868	990
GW	Hypochlorite	20	59	184	962	1,200
Total		20	120	320	991	2,234

Exhibit A.3: Chlorate DBP ICR Occurrence Data from Systems Required to Monitor – Summary of Samples

Source Water Type	Primary Disinfectant Type	Total Number of Samples	Number of Detections	Percent Detections	Number of Detections > HRL (210 µg/L)	Percent of Detections > HRL (210 µg/L)	Number of Detections > 2xHRL (420 µg/L)	Percent of Detections > 2xHRL (420 µg/L)
SW	Hypochlorite	420	336	80.0%	87	20.7%	39	9.3%
SW	Chlorine Dioxide and Ozone	50	47	94.0%	45	90.0%	36	72.0%
SW	Chlorine Dioxide	1,063	974	91.6%	184	17.3%	20	1.9%
SW	Ozone	53	37	69.8%	9	17.0%	2	3.8%
GW	Hypochlorite	133	96	72.2%	7	5.3%	4	3.0%
Total		1,719	1,490	86.7%	332	19.3%	101	5.9%

Exhibit A.4: Chlorate DBP ICR Occurrence Data – Summary of System and Population Served Data from Systems Required to Monitor – All Detections

Source Water Type	Primary Disinfectant Type	Total Number of Systems	Total Population Served by Systems	Number of Systems with Detections	Population Served by Systems with Detections	Percent of Systems with Detections	Percent of Population Served by Systems with Detections
SW	Hypochlorite	49	30,972,523	44	25,871,147	89.8%	83.5%
SW	Chlorine Dioxide and Ozone	1	223,411	1	223,411	100%	100%
SW	Chlorine Dioxide	21	5,947,815	21	5,947,815	100%	100%
SW	Ozone	8	5,156,001	8	5,156,001	100%	100%
GW	Hypochlorite	17	6,146,635	17	6,146,635	100%	100%
Total		82	41,584,457	80	37,828,450	97.6%	91.0%

Note: Systems that had changes in disinfection practices are counted in multiple rows. Therefore the numbers in the table do not add up to the value in the "total" row.

Exhibit A.5: Chlorate DBP ICR Occurrence Data – Summary of System and Population Served Data from Systems Required to Monitor – Detections > HRL

Source Water Type	Primary Disinfectant Type	Total Number of Systems	Total Population Served by Systems	Number of Systems with Detections > HRL (210 µg/L)	Population Served by Systems with Detections > HRL (210 µg/L)	Percent of Systems with Detections > HRL (210 µg/L)	Percent of Population Served by Systems with Detections > HRL (210 µg/L)
SW	Hypochlorite	49	30,972,523	18	7,335,757	36.7%	23.7%
SW	Chlorine Dioxide and Ozone	1	223,411	1	223,411	100%	100%
SW	Chlorine Dioxide	21	5,947,815	14	3,773,354	66.7%	63.4%
SW	Ozone	8	5,156,001	4	3,749,231	50.0%	72.7%
GW	Hypochlorite	17	6,146,635	3	481,489	17.6%	7.8%
Total		82	41,584,457	34	11,824,489	41.5%	28.4%

Note: Systems that had changes in disinfection practices are counted in multiple rows. Therefore, the numbers in the table do not add up to the value in the "total" row.

Exhibit A.6: Chlorate DBP ICR Occurrence Data – Summary of System and Population Served Data from Systems Required to Monitor – Detections > 2xHRL

Source Water Type	Primary Disinfectant Type	Total Number of Systems	Total Population Served by Systems	Number of Systems with Detections > 2xHRL (420 µg/L)	Population Served by Systems with Detections > 2xHRL (420 μg/L)	Percent of Systems with Detections > 2xHRL (420 μg/L)	Percent of Population Served by Systems with Detections > 2xHRL (420 µg/L)
SW	Hypochlorite	49	30,972,523	5	2,016,629	10.2%	6.5%
SW	Chlorine Dioxide and Ozone	1	223,411	1	223,411	100%	100%
SW	Chlorine Dioxide	21	5,947,815	6	1,656,548	28.6%	27.9%
SW	Ozone	8	5,156,001	1	1,200,000	12.5%	23.3%
GW	Hypochlorite	17	6,146,635	1	156,450	5.9%	2.5%
Total		82	41,584,457	11	3,594,305	13.4%	8.6%

Note: Systems that had changes in disinfection practices are counted in multiple rows. Therefore, the numbers in the table do not add up to the value in the "total" row.

A.1.2 Limitations of DBP ICR Data

The DBP ICR was designed to gather chlorate monitoring data from very large systems (those serving over 100,000 customers) using hypochlorite or chlorine dioxide, two disinfectants known to be capable of generating chlorate as a DBP, in 1997-1998. Subsequent monitoring (see discussion of UCMR 3 in Chapter 5) has demonstrated that chlorate also sometimes occurs at systems using other disinfectants (or no disinfection at all). Therefore, DBP ICR results should not be interpreted as capturing chlorate occurrence at all very large systems. DBP ICR does not provide an indication of occurrence at systems serving 100,000 or fewer customers.

Interpretation of DBP ICR results is complicated by a lack of documented responsiveness to chlorate monitoring requirements. As noted above, it cannot be ruled out that some chlorate samples were collected and reported from systems that used neither hypochlorite nor chlorine dioxide and misunderstood the reporting requirements. Nor has EPA verified that all very large systems required to monitor for chlorate did monitor.

Since chlorate was only measured quarterly in systems using hypochlorite, it is also possible that fluctuations in concentrations were missed. Also, maximum residence times may not correspond well with locations of chlorine boosting stations, which are more likely to use hypochlorite due to logistical considerations.

A.2 Community Water System Survey (CWSS), 2006

The 2006 CWSS (USEPA, 2009b) gathered data on the financial and operating characteristics of a random sample of community water systems (CWSs) nationwide. All systems serving more than 500,000 people (94 systems in 2006) received the survey, and systems in that size category

were asked questions about concentrations of unregulated contaminants in their raw and finished water. Of the 94 systems asked about unregulated contaminants, 62 percent (58 systems) responded to the survey, though not all of these systems answered every question. EPA supplemented the data set by gathering additional information about contaminant occurrence at the 94 systems from publicly available sources (e.g., Consumer Confidence Reports (CCRs)).

In the 2006 CWSS, three of the 94 systems serving more than 500,000 people reported monitoring data for chlorate. A total of four chlorate samples were reported from these systems. Chlorate was detected in two (50 percent) of the four samples, at concentrations of 34 μ g/L and 51 μ g/L, which were both below the HRL. Reporting levels were not specified in this survey.

A.3 Environmental Working Group (EWG) Drinking Water Database, 2004-2009

In December 2009, EWG released its "National Drinking Water Database," which includes data on occurrence of drinking water contaminants (regulated and unregulated) collected between 2004 and 2009 from 45 states and the District of Columbia (EWG, 2015). The EWG database includes results from approximately 48,000 water systems; data were obtained primarily from state water offices.

EWG reviewed the data for inconsistencies, potential outliers and other errors. EWG also invited the American Water Works Association (AWWA) and the Association of Metropolitan Water Agencies (AMWA) to review the data and/or have their constituents, the PWSs, review the data. Some edits and corrections may have been made since the public release of the data in December, 2009. EPA's analysis is based solely on the data made publicly available by EWG on its Web site as of September, 2015. Reporting levels are not specified in EWG's database.

A total of 58 systems reported having tested for chlorate between 2004 and 2009. These data showed detections of chlorate in 44 (75.86 percent) of the PWSs, serving 11.7 million people in six states (Exhibit A.7). Of the ten PWSs with the highest study-wide average concentrations of chlorate, all ten had at least one daily average concentrations of chlorate that exceeded the HRL of 210 μ g/L. (Daily averages include both detections and non-detections; non-detections are assumed equal to 0.) Five systems had at least one daily average concentration in excess of 420 μ g/L. The highest reported daily average concentration was 1,062 μ g/L.

The EWG data base has several limitations. It is a selection of drinking water data and not a random sample, so it might not be representative. The use of daily average concentrations obscures some variability in the data. Furthermore, there is no information about sampling locations in the distribution system or disinfection practices associated with data in the database.

State	Number of PWSs with Detections of Chlorate	Population served by PWSs with Detections of Chlorate
California	31	10,798,220
Virginia	9	536,066
Alabama	1	237,390
New York	1	54,269
Iowa	1	41,795
Minnesota	1	10,778
Total	44	11,678,518

Exhibit A.7: Summary	of EWG	Chlorate	Data,	2004-2009
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Appendix B Additional UCMR 3 Occurrence Analyses

This appendix presents additional analyses on the occurrence of chlorate based on the UCMR 3 data available as of July 2016. These analyses include a presentation of chlorate occurrence estimates for community water systems (CWSs) as compared to non-transient non-community water systems (NTNCWSs). In addition, estimates of the number of systems and sampling locations with at least one detection greater than four thresholds are included (Minimum Reporting Level (MRL), Health Reference Level (HRL), twice the HRL (2xHRL) and three times the HRL (3xHRL)), as well as estimates of the number of sampling locations with a locational running annual average (LRAA) greater than the same four thresholds. Furthermore, this appendix also contains analytical results for characterizing the national use of disinfectant types based on the UCMR 3 data.

B.1 Additional Analyses on Occurrence by System Type

As was discussed earlier, the majority of UCMR 3 results came from CWSs rather than NTNCWSs. Exhibit B.1 and Exhibit B.2 present a summary of chlorate results from CWSs. Exhibit B.3 and Exhibit B.4 present a summary of chlorate results from NTNCWSs. A very small percentage of the chlorate data were submitted by NTNCWSs (specifically, less than one percent of the number of samples and approximately two percent of systems serving only 0.3 percent of the overall population served by participating systems).

Number of Percent of Number of Percent of Number of Percent of Number of Percent of Total Samples Samples Samples Samples Samples Samples Samples Samples System Size and Number of with with with with with with with with Source Water Type Samples Detections Detections Detections Detections Detections Detections Detections Detections from CWSs ≥ MRL ≥MRL > HRL > HRL > 2xHRL > 2xHRL > 3xHRL > 3xHRL (20 µg/L) (20 µg/L) (210 µg/L) (210 µg/L) (420 µg/L) (420 µg/L) (630 µg/L) (630 µg/L) Small Ground Water 2.930 1.185 40.44% 440 15.02% 207 7.06% 104 3.55% Systems Small Surface Water 2.563 1,347 52.56% 488 19.04% 183 7.14% 83 3.24% Systems All Small Systems 5,493 2,532 46.10% 928 16.89% 390 7.10% 187 3.40% Large Ground Water 18,639 8,270 44.37% 12.27% 848 4.55% 411 2.21% 2.287 Systems Large Surface Water 26,989 57.91% 15.630 4,640 17.19% 1,546 5.73% 648 2.40% Systems All Large Systems 45,628 23.900 52.38% 6,927 15.18% 2,394 5.25% 1,059 2.32% Very Large Ground 2,849 1,874 65.78% 321 11.27% 95 3.33% 31 1.09% Water Systems Very Large Surface 7,901 5,638 71.36% 1,446 18.30% 446 5.64% 204 2.58% Water Systems All Very Large 10,750 7,512 69.88% 16.44% 5.03% 235 2.19% 1,767 541 Systems All Water Systems 61.871 33.944 54.86% 9.622 15.55% 3.325 5.37% 2.39% 1.481

Exhibit B.1: National Occurrence of Chlorate Based on UCMR 3 Data – Summary of Samples with Detections Greater than Threshold Values (Community Water Systems)

Exhibit B.2: Chlorate National Occurrence Measures Based on UCMR 3 Assessment Monitoring Data – Summary of System and Population Served Data – Detections in CWSs

System Size and Source Water Type	Number of UCMR 3 CWSs	Population Served by UCMR 3 CWSs	Number of UCMR 3 CWSs With At Least One Detection ≥ MRL	Population Served by UCMR 3 CWSs With At Least One Detection ≥ MRL	Percent of UCMR 3 CWSs With At Least One Detection ≥ MRL	Percent of Population Served by UCMR 3 CWSs With At Least One Detection ≥ MRL
Small Ground Water Systems	454	1,416,623	248	734,560	54.6%	51.9%
Small Surface Water Systems	256	1,197,079	177	807,221	69.1%	67.4%
All Small Systems	710	2,613,702	425	1,541,781	59.9%	59.0%
Large Ground Water Systems	1,440	36,890,862	877	24,317,497	60.9%	65.9%
Large Surface Water Systems	2,248	69,292,924	1,673	52,320,637	74.4%	75.5%
All Large Systems	3,688	106,183,786	2,550	76,638,134	69.1%	72.2%
Very Large Ground Water Systems	68	16,355,951	58	14,508,549	85.3%	88.7%
Very Large Surface Water Systems	339	114,955,260	293	98,329,514	86.4%	85.5%
All Very Large Systems	407	131,311,211	351	112,838,063	86.2%	85.9%
All Water Systems	4,805	240,108,699	3,326	191,017,978	69.2%	79.6%

System Size and Source Water Type	Total Number of Samples from NTNCWSs	Number of Samples with Detections ≥ MRL (20 μg/L)	Percent of Samples with Detections ≥ MRL (20 μg/L)	Number of Samples with Detections > HRL (210 µg/L)	Percent of Samples with Detections > HRL (210 µg/L)	Number of Samples with Detections > 2xHRL (420 µg/L)	Percent of Samples with Detections > 2xHRL (420 µg/L)	Number of Samples with Detections > 3xHRL (630 µg/L)	Percent of Samples with Detections > 3xHRL (630 µg/L)
Small Ground Water Systems	308	107	34.74%	53	17.21%	27	8.77%	17	5.52%
Small Surface Water Systems	135	122	90.37%	46	34.07%	25	18.52%	19	14.07%
All Small Systems	443	229	51.69%	99	22.35%	52	11.74%	36	8.13%
Large Ground Water Systems	58	41	70.69%	10	17.24%	3	5.17%	2	3.45%
Large Surface Water Systems	30	22	73.33%	10	33.33%	3	10.00%	1	3.33%
All Large Systems	88	63	71.59%	20	22.73%	6	6.82%	3	3.41%
Very Large Ground Water Systems	0	0	0.00%	0	0.00%	0	0.00%	0	0.00%
Very Large Surface Water Systems	12	3	25.00%	0	0.00%	0	0.00%	0	0.00%
All Very Large Systems	12	3	25.00%	0	0.00%	0	0.00%	0	0.00%
All Water Systems	543	295	54.33%	119	21.92%	58	10.68%	39	7.18%

Exhibit B.3: National Occurrence of Chlorate Based on UCMR 3 Data – Summary of Samples with Detections Greater than Threshold Values (Non-Transient Non-Community Water Systems)

Exhibit B.4: Chlorate National Occurrence Measures Based on UCMR 3 Assessment Monitoring Data – Summary of System and Population Served Data – Detections in NTNCWSs

System Size and Source Water Type	Number of UCMR 3 NTNCWSs	Population Served by UCMR 3 NTNCWSs	Number of UCMR 3 NTNCWSs With At Least One Detection ≥ MRL	Population Served by UCMR 3 NTNCWSs With At Least One Detection ≥ MRL	Percent of UCMR 3 NTNCWSs With At Least One Detection ≥ MRL	Percent of Population Served by UCMR 3 NTNCWSs With At Least One Detection ≥ MRL
Small Ground Water Systems	73	82,222	28	54,024	38.4%	65.7%
Small Surface Water Systems	16	53,136	16	53,136	100.0%	100.0%
All Small Systems	89	135,358	44	107,160	49.4%	79.2%
Large Ground Water Systems	9	185,929	7	163,029	77.8%	87.7%
Large Surface Water Systems	4	160,896	3	111,413	75.0%	69.2%
All Large Systems	13	346,825	10	274,442	76.9%	79.1%
Very Large Ground Water Systems	0	0	0	0	0.0%	0.0%
Very Large Surface Water Systems	1	203,000	1	203,000	100.0%	100.0%
All Very Large Systems	1	203,000	1	203,000	100.0%	100.0%
All Water Systems	103	685,183	55	584,602	53.4%	85.3%

B.2 Analyses on Samples with Detections

This appendix shows analyses of chlorate concentrations at EP and MR locations using the UCMR 3 data. Exhibit B.5 shows a statistical summary of reported chlorate concentrations by system size and source water type (including the minimum, median, maximum, 90th percentile and 99th percentile). The remaining exhibits in this section show chlorate concentrations expressed as a percentage of systems, samples, or sampling locations with at least one detection greater than a given threshold. A sample-level summary of the results relative to the MRL, HRL, twice the HRL (2xHRL) and three times the HRL (3xHRL) is presented in Exhibit B.6. Simple detections are evaluated on a "greater than or equal to" basis (\geq the MRL), while healthbased thresholds are evaluated in terms of exceedances (> HRL, > 2xHRL, and > 3xHRL). Exhibit B.7 through Exhibit B.10 show more detailed system-level results, including national extrapolations for small systems, at the same four thresholds. These tables summarize the number of systems and associated population served with at least one detection greater than each threshold. Figures for large and very large systems represent a census of systems in those categories. No extrapolation was necessary in these categories, as it was for the small systems, to derive national estimates of occurrence in these exhibits. National estimates of occurrence are reported separately in each system size and source water category, and also in aggregate. Exhibit B.11 through Exhibit B.14 show the equivalent results for monitoring locations rather than systems (making an assumption that each system's population is equally distributed among its several sampling locations, as described in more detail below). Exhibit B.15 presents a summary of additional nationally extrapolated results at the system level and sample location level at the four thresholds. It includes system-level national population estimates.

Reported chlorate concentrations range from 20 μ g/L (the MRL) to 22,000 μ g/L (Exhibit B.5). As of July 2016, a total of 62,414 chlorate samples had been collected from 4,908 systems. As shown in Exhibit B.6, of these samples, 9,741 (15.6 percent) reported at least one detection exceeding the HRL of 210 μ g/L, 3,383 (5.4 percent) reported at least one detection exceeding twice the HRL (420 μ g/L) and 1,520 (2.4 percent) reported at least one detection exceeding three times the HRL (630 μ g/L).

Additional details of system-level findings at each threshold are presented in Exhibit B.7 through Exhibit B.10. These tables show that 1,887 (38.4 percent of UCMR 3 systems, serving 48.2 percent of the PWS-served population) reported at least one detection greater than the HRL of 210 μ g/L, 982 (20.0 percent of UCMR 3 systems, serving 24.9 percent of the PWS-served population) reported at least one detection greater than twice the HRL (420 μ g/L), and 558 (11.4 percent of UCMR 3 systems, serving 12.8 percent of the PWS-served population) reported at least one detection greater than three times the HRL (630 μ g/L). As summarized in Exhibit B.15, an estimated 22,497 PWSs serving between 79 and 134 million people nationally have at least one chlorate detection greater than the HRL, an estimated 11,757 PWSs serving between 32 and 68 million people nationally have at least one chlorate detection greater than three times the HRL. The derivation of these population ranges is described later in this section.

While the analyses presented in this appendix differentiate by system size, it is important to note that disinfectant type is a significant factor affecting chlorate occurrence and different system sizes can have different distributions of disinfectant types. See Section 5.5 for a breakdown of detections by system size and disinfection type.

System Size and Source Water Type	Minimum of Detected Concentrations (µg/L)	Median of Detected Concentrations (µg/L)	90 th Percentile of Detected Concentrations (µg/L)	99 th Percentile of Detected Concentrations (µg/L)	Maximum of Detected Concentrations (µg/L)
Small Ground Water Systems	20	150	598	2,635	7,208
Small Surface Water Systems	20	150	520	1,500	3,472
All Small Systems	20	150	559	1,840	7,208
Large Ground Water Systems	20	110	430	1,339	22,000
Large Surface Water Systems	20	130	420	1,100	13,600
All Large Systems	20	120	421	1,190	22,000
Very Large Ground Water Systems	20	74	300	700	1,658
Very Large Surface Water Systems	20	120	370	992	3,000
All Very Large Systems	20	110	360	970	3,000
All Water Systems	20	120	420	1,200	22,000

Exhibit B.5: Chlorate Occurrence Data from UCMR 3 - Summary of Detected Concentrations

System Size and Source Water Type	Total Number of Samples	Number of Samples with Detections ≥ MRL (20 μg/L)	Percent of Samples with Detections ≥ MRL (20 μg/L)	Number of Samples with Detections > HRL (210 µg/L)	Percent of Samples with Detections > HRL (210 μg/L)	Number of Samples with Detections > 2xHRL (420 µg/L)	Percent of Samples with Detections > 2xHRL (420 μg/L)	Number of Samples with Detections > 3xHRL (630 µg/L)	Percent of Samples with Detections > 3xHRL (630 μg/L)
Small Ground Water Systems	3,238	1,292	39.90%	493	15.23%	234	7.23%	121	3.74%
Small Surface Water Systems	2,698	1,469	54.45%	534	19.79%	208	7.71%	102	3.78%
All Small Systems	5,936	2,761	46.51%	1,027	17.30%	442	7.45%	223	3.76%
Large Ground Water Systems	18,697	8,311	44.45%	2,297	12.29%	851	4.55%	413	2.21%
Large Surface Water Systems	27,019	15,652	57.93%	4,650	17.21%	1,549	5.73%	649	2.40%
All Large Systems	45,716	23,963	52.42%	6,947	15.20%	2,400	5.25%	1,062	2.32%
Very Large Ground Water Systems	2,849	1,874	65.78%	321	11.27%	95	3.33%	31	1.09%
Very Large Surface Water Systems	7,913	5,641	71.29%	1,446	18.27%	446	5.64%	204	2.58%
All Very Large Systems	10,762	7,515	69.83%	1,767	16.42%	541	5.03%	235	2.18%
All Water Systems	62,414	34,239	54.86%	9,741	15.61%	3,383	5.42%	1,520	2.44%

Exhibit B.6: National Occurrence of Chlorate Based on UCMR 3 Data - Summary of Samples with Detections Greater than Threshold Values

Percent of National National Number of Population Estimate of Population Percent of Estimate UCMR 3 Served by UCMR 3 Served by National Population Population National of Number of Systems UCMR 3 UCMR 3 Served by Systems Inventory of System Size and Source Served by Inventory Systems UCMR 3 With At With At Systems Systems Systems With Population Water Type UCMR 3 of With At With At With At Systems Least One At Least One Least One Served by Systems¹ Least One Systems System¹ Least One Detection Detection Detection Least One Detection ≥ MRL ≥ MRL ≥ MRL Detection Detection \geq MRL² ≥ MRL \geq MRL² Small Ground Water 527 1,498,845 276 788,584 52.4% 52.6% 55,700 38,730,597 29,171 20,377,243 **Systems** Small Surface Water 272 1,250,215 193 860,357 71.0% 68.8% 9,728 20,007,917 6,903 13,768,793 Systems All Small Systems 799 2,749,060 469 1,648,941 58.7% 60.0% 65,428 58,738,514 36,074 34,146,036 Large Ground Water 1.449 37.076.791 884 24.480.526 61.0% 66.0% 1.470 37,540,614 884 24,480,526 Systems Large Surface Water 2.252 69,453,820 1.676 52.432.050 74.4% 75.5% 2.310 70.791.005 1.676 52.432.050 Systems All Large Systems 3,701 106,530,611 2,560 76,912,576 69.2% 72.2% 3,780 108,331,619 2,560 76,912,576 Very Large Ground Water 68 16,355,951 58 14.508.549 85.3% 88.7% 68 16,355,951 58 14.508.549 Systems Verv Large Surface Water 340 115,158,260 294 98,532,514 86.5% 85.6% 343 120,785,622 294 98,532,514 **Systems** All Very Large Systems 408 131,514,211 352 113,041,063 86.3% 86.0% 411 137,141,573 352 113.041.063 All Water Systems 4.908 240,793,882 3.381 191,602,580 68.9% 79.6% 69.619 304,211,706 38.986 224,099,675

Exhibit B.7: National Occurrence and Exposure Based on UCMR 3 Data – Summary of System and Population Served Data – Detections of Chlorate

Source: UCMR 3 chlorate data available in July 2016 (USEPA, 2016e). UCMR 3 monitoring was required at a representative sample of small systems (serving <10,000 people) and at all large (serving 10,001 to 100,000 people) and very large systems (serving >100,000 people) systems in the nation.

¹ The small system national inventory numbers for systems and population served by systems were derived from a freeze of the December 2010 SDWIS/Fed data. These counts are based on all community and non-transient non-community water systems that served 10,000 people or fewer. All large and very large systems were required to conduct UCMR 3 Assessment Monitoring; thus, the national inventory numbers for the large and very large systems are based on the number of systems expected to complete UCMR 3 monitoring.

² National estimates for the small systems are generated by multiplying the UCMR 3 national statistical sample findings of system/population percentages and national system/population inventory numbers for PWSs. National estimates for the large and very large systems are based directly on the UCMR 3 results, since this was a census.

Exhibit B.8: National Occurrence and Exposure Based on UCMR 3 Data – Summary of System and Population Served Data – Detections of Chlorate > HRL (210 µg/L)

System Size and Source Water Type	Number of UCMR 3 Systems	Population Served by UCMR 3 Systems	Number of UCMR 3 Systems With At Least One Detection > HRL	Population Served by UCMR 3 Systems With At Least One Detection > HRL	Percent of UCMR 3 Systems With At Least One Detection > HRL	Percent of Population Served by UCMR 3 Systems With At Least One Detection > HRL	National Inventory of Systems ¹	National Inventory of Population Served by System ¹	National Estimate of Systems With At Least One Detection > HRL ²	National Estimate of Population Served by Systems With At Least One Detection > HRL ²
Small Ground Water Systems	527	1,498,845	160	399,068	30.4%	26.6%	55,700	38,730,597	16,911	10,312,035
Small Surface Water Systems	272	1,250,215	111	504,760	40.8%	40.4%	9,728	20,007,917	3,970	8,077,968
All Small Systems	799	2,749,060	271	903,828	33.9%	32.9%	65,428	58,738,514	20,881	18,390,002
Large Ground Water Systems	1,449	37,076,791	447	13,236,245	30.8%	35.7%	1,470	37,540,614	447	13,236,245
Large Surface Water Systems	2,252	69,453,820	935	29,762,039	41.5%	42.9%	2,310	70,791,005	935	29,762,039
All Large Systems	3,701	106,530,611	1,382	42,998,284	37.3%	40.4%	3,780	108,331,619	1,382	42,998,284
Very Large Ground Water Systems	68	16,355,951	40	10,734,989	58.8%	65.6%	68	16,355,951	40	10,734,989
Very Large Surface Water Systems	340	115,158,260	194	61,434,961	57.1%	53.3%	343	120,785,622	194	61,434,961
All Very Large Systems	408	131,514,211	234	72,169,950	57.4%	54.9%	411	137,141,573	234	72,169,950
All Water Systems	4,908	240,793,882	1,887	116,072,062	38.4%	48.2%	69,619	304,211,706	22,497	133,558,236

Source: UCMR 3 chlorate data available in July 2016 (USEPA, 2016e). UCMR 3 monitoring was required at a representative sample of small systems (serving <10,000 people) and at all large (serving 10,001 to 100,000 people) and very large systems (serving >100,000 people) systems in the nation.

¹ The small system national inventory numbers for systems and population served by systems were derived from a freeze of the December 2010 SDWIS/Fed data. These counts are based on all community and non-transient non-community water systems that served 10,000 people or fewer. All large and very large systems were required to conduct UCMR 3 Assessment Monitoring; thus, the national inventory numbers for the large and very large systems are based on the number of systems expected to complete UCMR 3 monitoring.

²National estimates for the small systems are generated by multiplying the UCMR 3 national statistical sample findings of system/population percentages and national system/population inventory numbers for PWSs. National estimates for the large and very large systems are based directly on the UCMR 3 results, since this was a census.

Exhibit B.9: National Occurrence and Exposure Based on UCMR 3 Data – Summary of System and Population Served Data – Detections of Chlorate > 2xHRL (420 µg/L)

System Size and Source Water Type	Number of UCMR 3 Systems	Population Served by UCMR 3 Systems	Number of UCMR 3 Systems With At Least One Detection > 2xHRL	Population Served by UCMR 3 Systems With At Least One Detection > 2xHRL	Percent of UCMR 3 Systems With At Least One Detection > 2xHRL	Percent of Population Served by UCMR 3 Systems With At Least One Detection > 2xHRL	National Inventory of Systems ¹	National Inventory of Population Served by System ¹	National Estimate of Systems With At Least One Detection > 2xHRL ²	National Estimate of Population Served by Systems With At Least One Detection > 2xHRL ²
Small Ground Water Systems	527	1,498,845	83	184,230	15.7%	12.3%	55,700	38,730,597	8,772	4,760,558
Small Surface Water Systems	272	1,250,215	60	254,260	22.1%	20.3%	9,728	20,007,917	2,146	4,069,071
All Small Systems	799	2,749,060	143	438,490	17.9%	16.0%	65,428	58,738,514	10,918	8,829,628
Large Ground Water Systems	1,449	37,076,791	256	7,813,505	17.7%	21.1%	1,470	37,540,614	256	7,813,505
Large Surface Water Systems	2,252	69,453,820	460	14,077,954	20.4%	20.3%	2,310	70,791,005	460	14,077,954
All Large Systems	3,701	106,530,611	716	21,891,459	19.3%	20.5%	3,780	108,331,619	716	21,891,459
Very Large Ground Water Systems	68	16,355,951	24	6,838,332	35.3%	41.8%	68	16,355,951	24	6,838,332
Very Large Surface Water Systems	340	115,158,260	99	30,829,946	29.1%	26.8%	343	120,785,622	99	30,829,946
All Very Large Systems	408	131,514,211	123	37,668,278	30.1%	28.6%	411	137,141,573	123	37,668,278
All Water Systems	4,908	240,793,882	982	59,998,227	20.0%	24.9%	69,619	304,211,706	11,757	68,389,365

Source: UCMR 3 chlorate data available in July 2016 (USEPA, 2016e). UCMR 3 monitoring was required at a representative sample of small systems (serving <10,000 people) and at all large (serving 10,001 to 100,000 people) and very large systems (serving >100,000 people) systems in the nation.

¹ The small system national inventory numbers for systems and population served by systems were derived from a freeze of the December 2010 SDWIS/Fed data. These counts are based on all community and non-transient non-community water systems that served 10,000 people or fewer. All large and very large systems were required to conduct UCMR 3 Assessment Monitoring; thus, the national inventory numbers for the large and very large systems are based on the number of systems expected to complete UCMR 3 monitoring.

²National estimates for the small systems are generated by multiplying the UCMR 3 national statistical sample findings of system/population percentages and national system/population inventory numbers for PWSs. National estimates for the large and very large systems are based directly on the UCMR 3 results, since this was a census.

Percent of National National Number of Population Percent of Population Estimate of Estimate UCMR 3 Served by UCMR 3 Served by National Population Population National of Number of Systems UCMR 3 Systems UCMR 3 Inventory of Served by System Size and Source Served by Inventorv Systems UCMR 3 With At Systems With With At Systems Population Systems Water Type UCMR 3 of With At Systems Least One At Least One Least One With At Served by With At Least One Systems Systems¹ Detection Detection Detection Least One System¹ Least One Detection > 3xHRL > 3xHRL > 3xHRL Detection Detection $> 3 \times HRL^2$ > 3xHRL > 3xHRL² Small Ground Water 527 1,498,845 47 89,473 8.9% 6.0% 55,700 38,730,597 4,968 2,312,009 Systems Small Surface Water 272 1,250,215 36 121,852 13.2% 9.7% 9,728 20,007,917 1,288 1,950,068 Systems All Small Systems 799 2,749,060 83 211,325 10.4% 7.7% 65,428 58,738,514 6,255 4,262,077 Large Ground Water 1.449 37.076.791 161 4.950.177 11.1% 13.4% 1.470 37.540.614 161 4.950.177 Systems Large Surface Water 2.252 69,453,820 248 7,450,699 11.0% 10.7% 2,310 70,791,005 248 7,450,699 Systems All Large Systems 3.701 106.530.611 409 12.400.876 11.1% 11.6% 3.780 108.331.619 409 12.400.876 Very Large Ground Water 68 16,355,951 12 3,062,099 17.6% 18.7% 68 16,355,951 12 3,062,099 Systems Verv Large Surface Water 340 115.158.260 54 15,193,581 15.9% 13.2% 343 120,785,622 54 15,193,581 Systems All Very Large Systems 408 131,514,211 66 18,255,680 16.2% 13.9% 411 137,141,573 66 18,255,680 240,793,882 30,867,881 All Water Systems 4.908 558 11.4% 12.8% 69,619 304,211,706 6,730 34,918,633

Exhibit B.10: National Occurrence and Exposure Based on UCMR 3 Data – Summary of System and Population Served Data – Detections of Chlorate > 3xHRL (630 µg/L)

Source: UCMR 3 chlorate data available in July 2016 (USEPA, 2016e). UCMR 3 monitoring was required at a representative sample of small systems (serving <10,000 people) and at all large (serving 10,001 to 100,000 people) and very large systems (serving >100,000 people) systems in the nation.

¹ The small system national inventory numbers for systems and population served by systems were derived from a freeze of the December 2010 SDWIS/Fed data. These counts are based on all community and non-transient non-community water systems that served 10,000 people or fewer. All large and very large systems were required to conduct UCMR 3 Assessment Monitoring; thus, the national inventory numbers for the large and very large systems are based on the number of systems expected to complete UCMR 3 monitoring.

²National estimates for the small systems are generated by multiplying the UCMR 3 national statistical sample findings of system/population percentages and national system/population inventory numbers for PWSs. National estimates for the large and very large systems are based directly on the UCMR 3 results, since this was a census.

Exhibit B.11: National Occurrence and Exposure Based on UCMR 3 Data – Summary of Sampling Locations and Proportional Population Served Data – Detections of Chlorate

System Size and Source Water Type	Number of UCMR 3 Sample Locations	Population Served by UCMR 3 Sample Locations	Number of UCMR 3 Sample Locations With At Least One Detection	Population Served by UCMR 3 Sample Locations With At Least One Detection	Percent of UCMR 3 Sample Locations With At Least One Detection	Percent of Population Served by UCMR 3 Sample Locations With At Least One Detection	National Inventory of Sample Locations ¹	National Inventory of Population Served by Sample Locations ¹	National Estimate of Sample Locations With At Least One Detection	National Estimate of Population Served by Sample Locations With At Least One Detection
Small Ground Water Systems	1,632	1,498,845	741	693,639	45.4%	46.3%	110,647	38,730,597	50,238	17,923,829
Small Surface Water Systems	762	1,250,215	476	757,170	62.5%	60.6%	16,759	20,007,917	10,469	12,117,428
All Small Systems	2,394	2,749,060	1,217	1,450,808	50.8%	52.8%	127,405	58,738,514	60,707	30,041,257
Large Ground Water Systems	9,584	37,076,791	4,705	19,576,322	49.1%	52.8%	9,584	37,076,791	4,705	19,576,322
Large Surface Water Systems	8,595	69,453,820	5,604	45,539,999	65.2%	65.6%	8,595	69,453,820	5,604	45,539,999
All Large Systems	18,179	106,530,611	10,309	65,116,321	56.7%	61.1%	18,179	106,530,611	10,309	65,116,321
Very Large Ground Water Systems	1,446	16,355,951	1,032	11,224,224	71.4%	68.6%	1,446	16,355,951	1,032	11,224,224
Very Large Surface Water Systems	2,866	115,158,260	2,189	78,034,002	76.4%	67.8%	2,866	115,158,260	2,189	78,034,002
All Very Large Systems	4,312	131,514,211	3,221	89,258,226	74.7%	67.9%	4,312	131,514,211	3,221	89,258,226
All Water Systems	24,885	240,793,882	14,747	155,825,356	59.3%	64.7%	149,896	296,783,336	74,237	184,415,804

Source: UCMR 3 chlorate data available in July 2016 (USEPA, 2016e). UCMR 3 monitoring was required at a representative sample of small systems (serving <10,000 people) and at all large (serving 10,001 to 100,000 people) and very large systems (serving >100,000 people) systems in the nation.

Exhibit B.12: National Occurrence and Exposure Based on UCMR 3 Data – Summary of Sampling Locations and Proportional Population Served Data – Detections of Chlorate > HRL (210 µg/L)

System Size and Source Water Type	Number of UCMR 3 Sample Locations	Population Served by UCMR 3 Sample Locations	Number of UCMR 3 Sample Locations With At Least One Detection > HRL	Population Served by UCMR 3 Sample Locations With At Least One Detection > HRL	Percent of UCMR 3 Sample Locations With At Least One Detection > HRL	Percent of Population Served by UCMR 3 Sample Locations With At Least One Detection > HRL	National Inventory of Sample Locations ¹	National Inventory of Population Served by Sample Locations ¹	National Estimate of Sample Locations With At Least One Detection > HRL	National Estimate of Population Served by Sample Locations With At Least One Detection > HRL
Small Ground Water Systems	1,632	1,498,845	356	292,785	21.8%	19.5%	110,647	38,730,597	24,136	7,565,661
Small Surface Water Systems	762	1,250,215	237	401,436	31.1%	32.1%	16,759	20,007,917	5,212	6,424,411
All Small Systems	2,394	2,749,060	593	694,221	24.8%	25.3%	127,405	58,738,514	29,348	13,990,072
Large Ground Water Systems	9,584	37,076,791	1,634	8,569,088	17.0%	23.1%	9,584	37,076,791	1,634	8,569,088
Large Surface Water Systems	8,595	69,453,820	2,334	20,173,198	27.2%	29.0%	8,595	69,453,820	2,334	20,173,198
All Large Systems	18,179	106,530,611	3,968	28,742,285	21.8%	27.0%	18,179	106,530,611	3,968	28,742,285
Very Large Ground Water Systems	1,446	16,355,951	226	5,595,636	15.6%	34.2%	1,446	16,355,951	226	5,595,636
Very Large Surface Water Systems	2,866	115,158,260	811	30,225,347	28.3%	26.2%	2,866	115,158,260	811	30,225,347
All Very Large Systems	4,312	131,514,211	1,037	35,820,984	24.0%	27.2%	4,312	131,514,211	1,037	35,820,984
All Water Systems	24,885	240,793,882	5,598	65,257,490	22.5%	27.1%	149,896	296,783,336	34,353	78,553,340

Source: UCMR 3 chlorate data available in July 2016 (USEPA, 2016e). UCMR 3 monitoring was required at a representative sample of small systems (serving <10,000 people) and at all large (serving 10,001 to 100,000 people) and very large systems (serving >100,000 people) systems in the nation.

Exhibit B.13: National Occurrence and Exposure Based on UCMR 3 Data – Summary of Sampling Locations and Proportional Population Served Data – Detections of Chlorate > 2xHRL (420 µg/L)

System Size and Source Water Type	Number of UCMR 3 Sample Locations	Population Served by UCMR 3 Sample Locations	Number of UCMR 3 Sample Locations With At Least One Detection > 2xHRL	Population Served by UCMR 3 Sample Locations With At Least One Detection > 2xHRL	Percent of UCMR 3 Sample Locations With At Least One Detection > 2xHRL	Percent of Population Served by UCMR 3 Sample Locations With At Least One Detection > 2xHRL	National Inventory of Sample Locations ¹	National Inventory of Population Served by Sample Locations ¹	National Estimate of Sample Locations With At Least One Detection > 2xHRL	National Estimate of Population Served by Sample Locations With At Least One Detection > 2xHRL
Small Ground Water Systems	1,632	1,498,845	173	116,958	10.6%	7.8%	110,647	38,730,597	11,729	3,022,219
Small Surface Water Systems	762	1,250,215	119	175,139	15.6%	14.0%	16,759	20,007,917	2,617	2,802,858
All Small Systems	2,394	2,749,060	292	292,097	12.2%	10.6%	127,405	58,738,514	14,346	5,825,077
Large Ground Water Systems	9,584	37,076,791	716	4,074,423	7.5%	11.0%	9,584	37,076,791	716	4,074,423
Large Surface Water Systems	8,595	69,453,820	946	8,243,509	11.0%	11.9%	8,595	69,453,820	946	8,243,509
All Large Systems	18,179	106,530,611	1,662	12,317,932	9.1%	11.6%	18,179	106,530,611	1,662	12,317,932
Very Large Ground Water Systems	1,446	16,355,951	82	1,953,161	5.7%	11.9%	1,446	16,355,951	82	1,953,161
Very Large Surface Water Systems	2,866	115,158,260	291	11,606,516	10.2%	10.1%	2,866	115,158,260	291	11,606,516
All Very Large Systems	4,312	131,514,211	373	13,559,677	8.7%	10.3%	4,312	131,514,211	373	13,559,677
All Water Systems	24,885	240,793,882	2,327	26,169,706	9.4%	10.9%	149,896	296,783,336	16,381	31,702,686

Source: UCMR 3 chlorate data available in July 2016 (USEPA, 2016e). UCMR 3 monitoring was required at a representative sample of small systems (serving <10,000 people) and at all large (serving 10,001 to 100,000 people) and very large systems (serving >100,000 people) systems in the nation.

Exhibit B.14: National Occurrence and Exposure Based on UCMR 3 Data – Summary of Sampling Locations and Proportional Population Served Data – Detections of Chlorate > 3xHRL (630 µg/L)

System Size and Source Water Type	Number of UCMR 3 Sample Locations	Population Served by UCMR 3 Sample Locations	Number of UCMR 3 Sample Locations With At Least One Detection > 3xHRL	Population Served by UCMR 3 Sample Locations With At Least One Detection > 3xHRL	Percent of UCMR 3 Sample Locations With At Least One Detection > 3xHRL	Percent of Population Served by UCMR 3 Sample Locations With At Least One Detection > 3xHRL	National Inventory of Sample Locations ¹	National Inventory of Population Served by Sample Locations ¹	National Estimate of Sample Locations With At Least One Detection > 3xHRL	National Estimate of Population Served by Sample Locations With At Least One Detection > 3xHRL
Small Ground Water Systems	1,632	1,498,845	99	56,782	6.1%	3.8%	110,647	38,730,597	6,712	1,467,266
Small Surface Water Systems	762	1,250,215	65	73,804	8.5%	5.9%	16,759	20,007,917	1,430	1,181,126
All Small Systems	2,394	2,749,060	164	130,586	6.9%	4.8%	127,405	58,738,514	8,142	2,648,391
Large Ground Water Systems	9,584	37,076,791	372	2,241,580	3.9%	6.0%	9,584	37,076,791	372	2,241,580
Large Surface Water Systems	8,595	69,453,820	431	3,604,117	5.0%	5.2%	8,595	69,453,820	431	3,604,117
All Large Systems	18,179	106,530,611	803	5,845,697	4.4%	5.5%	18,179	106,530,611	803	5,845,697
Very Large Ground Water Systems	1,446	16,355,951	29	677,853	2.0%	4.1%	1,446	16,355,951	29	677,853
Very Large Surface Water Systems	2,866	115,158,260	143	5,058,507	5.0%	4.4%	2,866	115,158,260	143	5,058,507
All Very Large Systems	4,312	131,514,211	172	5,736,360	4.0%	4.4%	4,312	131,514,211	172	5,736,360
All Water Systems	24,885	240,793,882	1,139	11,712,643	4.6%	4.9%	149,896	296,783,336	9,117	14,230,448

Source: UCMR 3 chlorate data available in July 2016 (USEPA, 2016e). UCMR 3 monitoring was required at a representative sample of small systems (serving <10,000 people) and at all large (serving 10,001 to 100,000 people) and very large systems (serving >100,000 people) systems in the nation.

Exhibit B.15 presents a summary of the national estimates of the number of PWSs, sampling locations and the population served by PWSs that had at least one detection of chlorate at or above the MRL and greater than the HRL, 2xHRL and 3xHRL. The third and fourth columns present a range of estimates of the population served by PWSs that had at least one detection of chlorate greater than the threshold. The two values in each population range represent a central value estimate and a high end estimate. The high end estimate of the population served was derived by adding the entire system population of all PWSs with at least one detection of chlorate above the threshold (see Exhibit B.7 through Exhibit B.10). EPA considers this a high end estimate because it is based on the assumption that the entire system population is served water from the sampling location that had the highest reported chlorate concentration. However, for the PWSs with multiple sampling locations, it is unlikely that the entire population served by the system would receive water from the one sampling location with the highest single concentration. Therefore, EPA also provides a central value estimate of the population served water with chlorate above a threshold (see Exhibit B.11 through Exhibit B.14). This central value estimate was developed by assuming that each system's population is equally distributed among its several sampling locations. With this assumption, the population served by a sampling location with at least one detection of chlorate above a given threshold is calculated by multiplying the system's total population served by the fraction of sampling locations with at least one detection of chlorate above that threshold.

Threshold Concentration	National Estimate of Number of PWSs with At Least One Detection > Threshold (Percent ¹)	National Estimate of Number of Sample Locations with At Least One Detection > Threshold (Percent ¹)	Estimated Range of Population Served by PWSs with At Least One Detection > Threshold (in millions)	Estimated Range of Percent Population Served by PWSs with At Least One Detection > Threshold ¹
≥ MRL (20 µg/L)	38,986 (56.0%)	74,237 (49.5%)	184 - 224	62.1% - 73.7%
> HRL (210 µg/L)	22,497 (32.3%)	34,353 (22.9%)	79 - 134	26.5% - 43.9%
> 2xHRL (420 µg/L)	11,757 (16.9%)	16,381 (10.9%)	32 - 68	10.7% - 22.5%
> 3xHRL (630 µg/L)	6,730 (9.7%)	9,117 (6.1%)	14 - 35	4.8% - 11.5%

Exhibit B.15: National Estimates of Systems and Population Served by Systems with At Least One Detection of Chlorate Greater than Threshold Values (Based on UCMR 3 Data)

Source: UCMR 3 chlorate data available in July 2016 (USEPA, 2016e).

¹ The estimated percentages of the national population exceeding the thresholds shown in this table are slightly different from the percentages of the UCMR 3 sample population exceeding the thresholds (which are shown in Exhibit B.7 through Exhibit B.14), reflecting the fact that the small systems are only a sample whereas the larger systems are taken as a census. These percentages are calculated by dividing the national estimate of systems/sampling locations/population served with threshold exceedances, shown in Exhibit B.7 through Exhibit B.14, by the national inventory of number of systems/sampling locations/population served, also shown in those exhibits.

Since participating systems reported data up to four times per year, UCMR 3 data can be used to perform an analysis of seasonal patterns in contaminant occurrence. EPA has not yet performed such an analysis for chlorate, but the U.S. Army Corps of Engineers (USACE) performed a seasonality analysis for chlorate using the partial UCMR 3 dataset posted in January 2015 (Gorzalski and Spiesman, 2015). USACE concluded that chlorate concentrations varied over the course of the year and were highest in the summer months. This seasonal pattern was more pronounced in systems with higher concentrations (at least one detection of chlorate in excess of the HRL of 210 μ g/L) than in those with lower concentrations. This was true for gaseous chlorine systems, on-site generation (OSG) hypochlorite systems, bulk hypochlorite solution systems and chlorine dioxide systems. Observing that the seasonal trend was less pronounced in chlorine dioxide systems, the study authors speculated that one reason for this may be that sensitivity to maximum regulatory concentration levels for chlorine dioxide and chlorite may limit the dose of chlorine dioxide used during the summer months. If systems lower chlorine dioxide doses to avoid higher chlorite levels, then the chlorate produced will also be lower during a time when higher temperatures would tend to increase concentrations.

B.3 Additional Analyses on Locational Averages

Exhibit B.16 through Exhibit B.18 show similar results as above at the four thresholds, but at the sample point level (i.e., the number of sample points and associated population served with detections greater than each threshold). As is discussed earlier in this report, for the purpose of calculating population exposure, each system's population was assumed to be equally distributed among its several sampling locations. With this assumption, the population served by a sampling location with an average concentration of chlorate above a given threshold is calculated by multiplying the system's total population served by the fraction of sampling locations with an average concentration of chlorate above that threshold.

Percent of National Number of Percent of National Population Population Estimate of UCMR 3 UCMR 3 Estimate Served by Served by National Population Population Sample Sample of Sample UCMR 3 UCMR 3 Served by Number of National Inventory of Served by Locations Locations Locations UCMR 3 Sample System Size and Source Sample Sample Inventorv Population UCMR 3 With With with Water Type Sample Locations With Locations of Sample Served by Locations Sample Locational Locational Locational Locations Locational With Locations¹ Sample with Locations Ave. Ave. Ave. Ave. Conc. Locational Locational Locations¹ Conc. Conc. Conc. > HRL Ave. Conc. Ave. Conc. > HRL > HRL > HRL > HRL > HRL Small Ground Water 1,632 1,498,845 265 209,929 16.2% 14.0% 110,647 38,730,597 17,966 5,424,626 Systems Small Surface Water 762 1,250,215 157 267,768 20.6% 21.4% 16,759 20,007,917 3,453 4,285,245 Systems All Small Systems 2,394 2,749,060 422 477.697 17.6% 17.4% 127,405 58,738,514 21,419 9,709,871 Large Ground Water 9.584 37.076.791 1.254 7.006.621 13.1% 18.9% 9.584 37.076.791 1.254 7.006.621 Systems Large Surface Water 8.595 69.453.820 1,509 12.610.558 17.6% 18.2% 8,595 69,453,820 1.509 12.610.558 Systems All Large Systems 18.179 106.530.611 2.763 19.617.179 15.2% 18.4% 18.179 106.530.611 2.763 19.617.179 Very Large Ground Water 1.446 16,355,951 162 3,880,974 11.2% 23.7% 16,355,951 3,880,974 1.446 162 Systems Verv Large Surface Water 2.866 115.158.260 524 18.511.111 18.3% 16.1% 2.866 115,158,260 524 18.511.111 Systems 131,514,211 All Very Large Systems 4.312 131,514,211 686 22,392,085 15.9% 17.0% 4,312 686 22,392,085 42,486,961 All Water Systems 24,885 240,793,882 3,871 15.6% 17.6% 149,896 296,783,336 24,868 51,719,135

Exhibit B.16: National Occurrence Based on UCMR 3 Data – Summary of Sample Locations – Locational Average Chlorate Concentration > HRL (210 µg/L)

Source: UCMR 3 chlorate data available in July 2016 (USEPA, 2016e). UCMR 3 monitoring was required at a representative sample of small systems (serving <10,000 people) and at all large (serving 10,001 to 100,000 people) and very large systems (serving >100,000 people) systems in the nation.

System Size and Source Water Type	Number of UCMR 3 Sample Locations	Population Served by UCMR 3 Sample Locations	Number of UCMR 3 Sample Locations With Locational Ave. Conc. > 2xHRL	Population Served by UCMR 3 Sample Locations With Locational Ave. Conc. > 2xHRL	Percent of UCMR 3 Sample Locations With Locational Ave. Conc. > 2xHRL	Percent of Population Served by UCMR 3 Sample Locations With Locational Ave. Conc. > 2xHRL	National Inventory of Sample Locations ¹	National Inventory of Population Served by Sample Locations ¹	National Estimate of Sample Locations with Locational Ave. Conc. > 2xHRL	National Estimate of Population Served by Sample Locations with Locational Ave. Conc. > 2xHRL
Small Ground Water Systems	1,632	1,498,845	116	67,553	7.1%	4.5%	110,647	38,730,597	7,865	1,745,600
Small Surface Water Systems	762	1,250,215	57	69,826	7.5%	5.6%	16,759	20,007,917	1,254	1,117,461
All Small Systems	2,394	2,749,060	173	137,379	7.2%	5.0%	127,405	58,738,514	9,118	2,863,061
Large Ground Water Systems	9,584	37,076,791	450	2,721,316	4.7%	7.3%	9,584	37,076,791	450	2,721,316
Large Surface Water Systems	8,595	69,453,820	411	3,332,774	4.8%	4.8%	8,595	69,453,820	411	3,332,774
All Large Systems	18,179	106,530,611	861	6,054,090	4.7%	5.7%	18,179	106,530,611	861	6,054,090
Very Large Ground Water Systems	1,446	16,355,951	36	944,185	2.5%	5.8%	1,446	16,355,951	36	944,185
Very Large Surface Water Systems	2,866	115,158,260	153	5,161,422	5.3%	4.5%	2,866	115,158,260	153	5,161,422
All Very Large Systems	4,312	131,514,211	189	6,105,607	4.4%	4.6%	4,312	131,514,211	189	6,105,607
All Water Systems	24,885	240,793,882	1,223	12,297,077	4.9%	5.1%	149,896	296,783,336	10,168	15,022,758

Exhibit B.17: National Occurrence Based on UCMR 3 – Summary of Sample Locations – Locational Average Chlorate Concentration > 2xHRL (420 µg/L)

Source: UCMR 3 chlorate data available in July 2016 (USEPA, 2016e). UCMR 3 monitoring was required at a representative sample of small systems (serving <10,000 people) and at all large (serving 10,001 to 100,000 people) and very large systems (serving >100,000 people) systems in the nation.

System Size and Source Water Type	Number of UCMR 3 Sample Locations	Population Served by UCMR 3 Sample Locations	Number of UCMR 3 Sample Locations With Locational Ave. Conc. > 3xHRL	Population Served by UCMR 3 Sample Locations With Locational Ave. Conc. > 3xHRL	Percent of UCMR 3 Sample Locations With Locational Ave. Conc. > 3xHRL	Percent of Population Served by UCMR 3 Sample Locations With Locational Ave. Conc. > 3xHRL	National Inventory of Sample Locations ¹	National Inventory of Population Served by Sample Locations ¹	National Estimate of Sample Locations with Locational Ave. Conc. > 3xHRL	National Estimate of Population Served by Sample Locations with Locational Ave. Conc. > 3xHRL
Small Ground Water Systems	1,632	1,498,845	60	36,190	3.7%	2.4%	110,647	38,730,597	4,068	935,164
Small Surface Water Systems	762	1,250,215	29	25,209	3.8%	2.0%	16,759	20,007,917	638	403,441
All Small Systems	2,394	2,749,060	89	61,400	3.7%	2.2%	127,405	58,738,514	4,706	1,338,605
Large Ground Water Systems	9,584	37,076,791	214	1,233,262	2.2%	3.3%	9,584	37,076,791	214	1,233,262
Large Surface Water Systems	8,595	69,453,820	134	1,021,164	1.6%	1.5%	8,595	69,453,820	134	1,021,164
All Large Systems	18,179	106,530,611	348	2,254,426	1.9%	2.1%	18,179	106,530,611	348	2,254,426
Very Large Ground Water Systems	1,446	16,355,951	10	150,738	0.7%	0.9%	1,446	16,355,951	10	150,738
Very Large Surface Water Systems	2,866	115,158,260	60	2,192,785	2.1%	1.9%	2,866	115,158,260	60	2,192,785
All Very Large Systems	4,312	131,514,211	70	2,343,523	1.6%	1.8%	4,312	131,514,211	70	2,343,523
All Water Systems	24,885	240,793,882	507	4,659,349	2.0%	1.9%	149,896	296,783,336	5,124	5,936,555

Exhibit B.18: National Occurrence Based on UCMR 3 – Summary of Sample Locations – Locational Average Chlorate Concentration > 3xHRL (630 µg/L)

Source: UCMR 3 chlorate data available in July 2016 (USEPA, 2016e). UCMR 3 monitoring was required at a representative sample of small systems (serving <10,000 people) and at all large (serving 10,001 to 100,000 people) and very large systems (serving >100,000 people) systems in the nation.

B.4 Analyses on Disinfectants Used

The UCMR 3 database provides a snapshot of disinfection practices in use at PWSs between 2013 and 2016. These findings help to inform the discussion of changes in disinfection practice over time presented in Section B.5 of this report.

The following exhibits (Exhibit B.19 through Exhibit B.23) illustrate the distribution of UCMR 3 sampling locations by disinfection technique(s) associated with samples at those sampling locations. Exhibit B.19 through Exhibit B.23 show the breakout across major categories by source water type, system size category and sampling location (EP and MR). Exhibit B.19 and Exhibit B.20 cover EP sampling locations, while Exhibit B.21 and Exhibit B.22 cover MR sampling locations. The first exhibit in each pair (i.e., Exhibit B.19 and Exhibit B.21 presents counts and percentages of sampling locations in select disinfection categories. Note that there is overlap between some of the categories in use in these two exhibits, reflecting the use of multiple disinfectants by some systems. The second exhibit in each pair (i.e., Exhibit B.20 and Exhibit B.22) presents counts and percentages of sampling locations in a set of more complex but mutually exclusive disinfection categories.

In both EP and MR locations, more than 30 percent of very large surface water systems (serving >100,000 people) use only chloramines or "chlorine and chloramines," while approximately 50 to 54 percent of very large surface water systems (serving >100,000 people) use chloramines alone or with another disinfectant such as ozone.

Exhibit B.23 presents an inventory of chlorate samples associated with various disinfectant codes and combinations of disinfectant codes. Counts in this table include samples from both EP and MR sampling locations.

Exhibit B.19: Use of Disinfectants by Source Water Type and System Size Based on UCMR 3 Data in EPs (select categories)

Sampling Location Source Water Type ¹	System size (population served)	Number of EPs	Count of EPs Indicating Exclusive Use of Chlorine (% of Total)	Count of EPs Indicating Exclusive Use of Chloramines, OR both Chlorine and Chloramines (% of Total)	Count of EPs Indicating Any Instance of Using Chlorine (% of Total)	Count of EPs Indicating Any Instance of Using Chloramines	Count of EPs Indicating Any Instance of Using Ozone (% of Total)	Count of EPs Indicating Any Instance of Using Chlorine Dioxide (% of Total)	Count of EPs Indicating Any Instance of Using UV Light (% of Total)	Count of EPs Indicating Any Instance of Using "Other Disinfectant" (% of Total)	Count of EPs Indicating "No Disinfectant Used" (% of Total)
GW	Small	992	690 (69.6%)	90 (9.1%)	803 (80.9%)	108 (10.9%)	1 (0.1%)	3 (0.3%)	5 (0.5%)	34 (3.4%)	127 (12.8%)
GW	Large	6,590	5,244 (79.6%)	602 (9.1%)	5,419 (82.2%)	620 (9.4%)	16 (0.2%)	37 (0.6%)	13 (0.2%)	97 (1.5%)	546 (8.3%)
GW	Very Large	2,256	1,947 (86.3%)	204 (9.0%)	2,017 (89.4%)	228 (10.1%)	28 (1.2%)	8 (0.4%)	2 (0.1%)	10 (0.4%)	55 (2.4%)
SW	Small	293	155 (52.9%)	75 (25.6%)	256 (87.4%)	101 (34.5%)	19 (6.5%)	33 (11.3%)	12 (4.1%)	8 (2.7%)	0 (0%)
SW	Large	2,257	1,240 (54.9%)	591 (26.2%)	1,594 (70.6%)	742 (32.9%)	130 (5.8%)	180 (8.0%)	92 (4.1%)	24 (1.1%)	35 (1.6%)
SW	Very Large	629	253 (40.2%)	213 (33.9%)	397 (63.1%)	317 (50.4%)	86 (13.7%)	53 (8.4%)	30 (4.8%)	5 (0.8%)	1 (0.2%)

Note: Based on EP locations with data posted from July 2016. UCMR 3 monitoring was required at a representative sample of small systems (serving <10,000 people) and at all large (serving 10,001 to 100,000 people) and very large systems (serving >100,000 people) systems in the nation.

1. The source water type of the sampling location (listed as "FacilityWaterType" in the UCMR 3 database) was used to develop these counts. The "SW" category includes "GU" and "MX".

The disinfection codes used to categorize each sampling location are provided graphically in the table header above each column. The legend to the right indicates what code or set of codes corresponds to each cell. Fully shaded cells show codes that must be present for a sampling location to be assigned to a category, and striped cells show codes that may be present. Blank cells show codes that must not be present. Because the categories shown in this table are neither exhaustive nor mutually exclusive, results do not add up to totals.

Layout K	еу	Color k	Key		
CLGA	CAGC	OZON	OTHD		Used
CLOF	CAOF	CLDO	NODU		May be used
and/or CLON	and/or CAON	UVLV			Not used

Exhibit B.20: Use of Disinfectants by Source Water Type and System Size Based on UCMR 3 Data in EPs (mutually exclusive categories)

Sampling Location Source Water Type ¹	System size (population served)	Number of EPs	Count of EPs Indicating Exclusive Use of Chlorine (% of Total)	Count of EPs Indicating Exclusive Use of Chloramines, OR both Chlorine and Chloramines (% of Total)	Count of EPs Indicating Any Instance of Chlorine Dioxide (Except in Combination with Ozone) (% of Total)	Count of EPs Indicating Any Instance of Ozone (Except in Combination with Chlorine Dioxide) (% of Total)	Count of EPs Indicating Any Instance of Chlorine Dioxide and Ozone in Combination (% of Total)	Count of EPs Indicating Any Instance of UV Light (Except in Combination with Chlorine Dioxide or Ozone) (% of Total)	Count of EPs Indicating Any Instance of Any Other Disinfectant or Combination of Disinfectants (% of Total)	Count of EPs Indicating "No Disinfectant Used" (% of Total)
GW	Small	992	690 (69.6%)	90 (9.1%)	3 (0.3%)	1 (0.1%)	0 (0%)	5 (0.5%)	76 (7.7%)	127 (12.8%)
GW	Large	6,590	5,244 (79.6%)	602 (9.1%)	35 (0.5%)	14 (0.2%)	2 (0%)	12 (0.2%)	135 (2.0%)	546 (8.3%)
GW	Very Large	2,256	1,947 (86.3%)	204 (9.0%)	8 (0.4%)	28 (1.2%)	0 (0%)	2 (0.1%)	12 (0.5%)	55 (2.4%)
SW	Small	293	155 (52.9%)	75 (25.6%)	32 (10.9%)	18 (6.1%)	1 (0.3%)	7 (2.4%)	5 (1.7%)	0 (0%)
SW	Large	2,257	1,240 (54.9%)	591 (26.2%)	176 (7.8%)	126 (5.6%)	4 (0.2%)	49 (2.2%)	36 (1.6%)	35 (1.6%)
SW	Very Large	629	253 (40.2%)	213 (33.9%)	50 (7.9%)	83 (13.2%)	3 (0.5%)	22 (3.5%)	4 (0.6%)	1 (0.2%)

Note: Based on EP locations with data posted from July 2016. UCMR 3 monitoring was required at a representative sample of small systems (serving <10,000 people) and at all large (serving 10,001 to 100,000 people) and very large systems (serving >100,000 people) systems in the nation.

1. The source water type of the sampling location (listed as "FacilityWaterType" in the UCMR 3 database) was used to develop these counts. The "SW" category includes "GU" and "MX".

The disinfection codes used to categorize each sampling location are provided graphically in the table header above each column. The legend to the right indicates what code or set of codes corresponds to each cell. Fully shaded cells show codes that must be present for a sampling location to be assigned to a category, and striped cells show codes that may be present. Blank cells show codes that must not be present. The categories shown in this table are mutually exclusive and encompass all the data, so results add up to totals.

Layout K	еу	_	Color Key			
CLGA	CAGC	OZON	OTHD			Used
CLOF	CAOF	CLDO	NODU			May be used
and/or CLON	and/or CAON	UVLV		4		Not used

Exhibit B.21: Use of Disinfectants by Source Water Type and System Size Based on UCMR 3 Data in MRs (select categories)

Sampling Location Source Water Type ¹	System size (population served)	Number of MRs	Count of MRs Indicating Exclusive Use of Chlorine (% of Total)	Count of MRs Indicating Exclusive Use of Chloramines, OR both Chlorine and Chloramines (% of Total)	Count of MRs Indicating Any Instance of Using Chlorine (% of Total)	Count of MRs Indicating Any Instance of Using Chloramines	Count of MRs Indicating Any Instance of Using Ozone (% of Total)	Count of MRs Indicating Any Instance of Using Chlorine Dioxide (% of Total)	Count of MRs Indicating Any Instance of Using UV Light (% of Total)	Count of MRs Indicating Any Instance of Using "Other Disinfectant" (% of Total)	Count of MRs Indicating "No Disinfectant Used" (% of Total)
GW	Small	710	535 (75.4%)	67 (9.4%)	596 (83.9%)	69 (9.7%)	1 (0.1%)	4 (0.6%)	5 (0.7%)	20 (2.8%)	75 (10.6%)
GW	Large	3,813	3,031 (79.5%)	435 (11.4%)	3,198 (83.9%)	450 (11.8%)	27 (0.7%)	34 (0.9%)	14 (0.4%)	50 (1.3%)	199 (5.2%)
GW	Very Large	697	555 (79.6%)	113 (16.2%)	596 (85.5%)	120 (17.2%)	13 (1.9%)	0 (0%)	1 (0.1%)	2 (0.3%)	7 (1.0%)
SW	Small	285	153 (53.7%)	74 (26.0%)	250 (87.7%)	99 (34.7%)	16 (5.6%)	30 (10.5%)	11 (3.9%)	9 (3.2%)	0 (0%)
SW	Large	2,176	1,163 (53.4%)	604 (27.8%)	1,513 (69.5%)	750 (34.5%)	128 (5.9%)	171 (7.9%)	91 (4.2%)	28 (1.3%)	29 (1.3%)
SW	Very Large	591	189 (32.0%)	218 (36.9%)	354 (59.9%)	322 (54.5%)	85 (14.4%)	68 (11.5%)	34 (5.8%)	5 (0.8%)	5 (0.8%)

Note: Based on MR locations with data posted from July 2016. UCMR 3 monitoring was required at a representative sample of small systems (serving <10,000 people) and at all large (serving 10,001 to 100,000 people) and very large systems (serving >100,000 people) systems in the nation.

1. The source water type of the sampling location (listed as "FacilityWaterType" in the UCMR 3 database) was used to develop these counts. The "SW" category includes "GU" and "MX".

The disinfection codes used to categorize each sampling location are provided graphically in the table header above each column. The legend to the right indicates what code or set of codes corresponds to each cell. Fully shaded cells show codes that must be present for a sampling location to be assigned to a category, and striped cells show codes that may be present. Blank cells show codes that must not be present. Because the categories shown in this table are neither exhaustive nor mutually exclusive, results do not add up to totals.

L	ayout K	ey				Color	Key
	CLGA	CAGC	OZON	OTHD			Used
	CLOF	CAOF	CLDO	NODU			May be
	and/or CLON	and/or CAON	UVLV		•		Not used

Exhibit B.22: Use of Disinfectants by Source Water Type and System Size Based on UCMR 3 Data in MRs (mutually exclusive categories)

Sampling Location Source Water Type ¹	System size (population served)	Number of MRs	Count of MRs Indicating Exclusive Use of Chlorine (% of Total)	Count of MRs Indicating Exclusive Use of Chloramines, OR both Chlorine and Chloramines (% of Total)	Count of MRs Indicating Any Instance of Chlorine Dioxide (Except in Combination with Ozone) (% of Total)	Count of MRs Indicating Any Instance of Ozone (Except in Combination with Chlorine Dioxide) (% of Total)	Count of MRs Indicating Any Instance of Chlorine Dioxide and Ozone in Combination (% of Total)	Count of MRs Indicating Any Instance of UV Light (Except in Combination with Chlorine Dioxide or Ozone) (% of Total)	Count of MRs Indicating Any Instance of Any Other Disinfectant or Combination of Disinfectants (% of Total)	Count of MRs Indicating "No Disinfectant Used" (% of Total)
GW	Small	710	535 (75.4%)	67 (9.4%)	4 (0.6%)	1 (0.1%)	0 (0%)	5 (0.7%)	23 (3.2%)	75 (10.6%)
GW	Large	3,813	3,031 (79.5%)	435 (11.4%)	30 (0.8%)	23 (0.6%)	4 (0.1%)	13 (0.3%)	78 (2.0%)	199 (5.2%)
GW	Very Large	697	555 (79.6%)	113 (16.2%)	0 (0%)	13 (1.9%)	0 (0%)	1 (0.1%)	8 (1.1%)	7 (1.0%)
SW	Small	285	153 (53.7%)	74 (26.0%)	30 (10.5%)	16 (5.6%)	0 (0%)	6 (2.1%)	6 (2.1%)	0 (0%)
SW	Large	2,176	1,163 (53.4%)	604 (27.8%)	166 (7.6%)	123 (5.7%)	5 (0.2%)	47 (2.2%)	39 (1.8%)	29 (1.3%)
SW	Very Large	591	189 (32.0%)	218 (36.9%)	65 (11.0%)	82 (13.9%)	3 (0.5%)	23 (3.9%)	6 (1.0%)	5 (0.8%)

Note: Based on MR locations with data posted from July 2016. UCMR 3 monitoring was required at a representative sample of small systems (serving <10,000 people) and at all large (serving 10,001 to 100,000 people) and very large systems (serving >100,000 people) systems in the nation.

1. The source water type of the sampling location (listed as "FacilityWaterType" in the UCMR 3 database) was used to develop these counts. The "SW" category includes "GU" and "MX".

The disinfection codes used to categorize each sampling location are provided graphically in the table header above each column. The legend to the right indicates what code or set of codes corresponds to each cell. Fully shaded cells show codes that must be present for a sampling location to be assigned to a category, and striped cells show codes that may be present. Blank cells show codes that must not be present. The categories shown in this table are mutually exclusive and encompass all the data, so results add up to totals.

Layout K	еу	Color Key			
CLGA	CAGC	OZON	OTHD		Used
CLOF	CAOF	CLDO	NODU		May be used
and/or CLON	and/or CAON	UVLV			Not used

Exhibit B.23: UCMR 3 Inventory of Chlorate Samples by Disinfectant Type

Sampling Location Source Water Type ¹	All Chlorate Samples	Chlorination: Gaseous chlorine only	Chlorination: OSG hypochlorite only	Chlorination: Bulk solution hypochlorite only	Chloramination: from gaseous chlorine only	Chloramination: from OSG hypochlorite only	Chloramination: from bulk solution hypochlorite only	Chlorine dioxide: alone and in any disinfectant combination	Chlorine dioxide: in combination with gaseous chlorine only	Chlorine dioxide: in combination with OSG hypochlorite only	Chlorine dioxide: in combination with bulk solution hypochlorite only
SW	27,975	6,339	966	4,496	3,244	724	1,546	1,743	576	48	173
GW	34,439	8,809	1,975	12,112	1,033	648	769	141	73	6	2
All	62,414	15,148	2,941	16,608	4,277	1,372	2,315	1,884	649	54	175
Sampling Location Source Water Type ¹	Ozonation: alone and in any disinfectant combination	Ozonation: in combination with gaseous chlorine only	Ozonation: in combination with OSG hypochlorite only	Ozonation: in combination with bulk solution hypochlorite only	UV light: alone and in any disinfectant combination	UV light: in combination with gaseous chlorine only	UV light: in combination with OSG hypochlorite only	UV light: in combination with bulk solution hypochlorite only	"Other disinfectant," alone and in any disinfectant combination	No disinfectant used (at least one NODU code, and no other codes)	Unknown disinfection status
Sampling Location Source Water Type ¹	Ozonation: alone and in any disinfectant combination	Ozonation: in combination with gaseous chlorine only	Ozonation: in combination with OSG hypochlorite only	Ozonation: in combination with bulk solution hypochlorite only	UV light: alone and in any disinfectant combination	UV light: in combination with gaseous chlorine only	UV light: in combination with OSG hypochlorite only	UV light: in combination with bulk solution hypochlorite only	"Other disinfectant," alone and in any disinfectant combination	No disinfectant used (at least one NODU code, and no other codes)	Unknown disinfection status
Sampling Location Source Water Type ¹	Ozonation: alone and in any disinfectant combination	Ozonation: in combination with gaseous chlorine only	Ozonation: in combination with OSG hypochlorite only 35	Ozonation: in combination with bulk solution hypochlorite only	UV light: alone and in any disinfectant combination	UV light: in combination with gaseous chlorine only	UV light: in combination with OSG hypochlorite only	UV light: in combination with bulk solution hypochlorite only	"Other disinfectant," alone and in any disinfectant combination	No disinfectant used (at least one NODU code, and no other codes)	Unknown disinfection status 5,099
Sampling Location Source Water Type ¹ SW	Ozonation: alone and in any disinfectant combination	Ozonation: in combination with gaseous chlorine only 178 32	Ozonation: in combination with OSG hypochlorite only 35 0	Ozonation: in combination with bulk solution hypochlorite only 153 39	UV light: alone and in any disinfectant combination	UV light: in combination with gaseous chlorine only 85 12	UV light: in combination with OSG hypochlorite only 16 2	UV light: in combination with bulk solution hypochlorite only 153 27	"Other disinfectant," alone and in any disinfectant combination 207 364	No disinfectant used (at least one NODU code, and no other codes) 291 2,009	Unknown disinfection status 5,099 5,903

Note: Counts include samples from both EPs and MRs. Based on UCMR 3 chlorate data available in July 2016 (USEPA, 2016e).

The disinfection codes used to categorize each sampling location are provided graphically in the table header above each column. The legend to the right indicates what code or set of codes corresponds to each cell. Fully shaded cells show codes that must be present for a sampling location to be assigned to a category, and striped cells show codes that may be present. Blank cells show codes that must not be present.

_ayout K	еу			C
CLGA	CAGC	OZON	OTHD	
CLOF	CAOF	CLDO	NODU	
CLON	CAON	UVLV		

Color	Key
	Used
	May be used
	Not used

Because the categories shown in this table are neither exhaustive nor mutually exclusive, results do not add up to totals.

OSG = on-site generated

1. The source water type of the sampling location (listed as "FacilityWaterType" in the UCMR 3 database) was used to develop these counts. The "SW" category includes "GU" and "MX".

B.5 Changes in Disinfection Practice

Changes in occurrence of chlorate need to be considered in combination with changes in disinfection practice. Changes in disinfection practice can be examined by comparing the disinfectant types listed in the DBP ICR data gathered in 1997-1998 (see Appendix A.1) and those listed in the UCMR 3 data gathered in 2013-2016. These data represent a time spread of nearly 20 years.

The mix of disinfection techniques used by the 199 common systems (those with occurrence data in both the DBP ICR and the UCMR 3) changed over the course of those two decades. The data shown in Exhibit B.24 suggest that exclusive use of gaseous chlorine diminished, while use of chlorine dioxide, ozone and ultraviolet light increased. Rates of chloramine use as a primary disinfectant stayed fairly stable, while chloramine use as a secondary disinfectant (to maintain a disinfectant residual in the distribution system) increased. Comparing the UCMR 3 dataset to findings from the previous round of the UCMR program, UCMR 2 (2008-2011), sheds additional light on the increasing trend in chloramination in recent years (Exhibit B.25). (Note that this exhibit presents a comparison of all chloraminating sample locations in each data set, not just those that are common to the two data sets.) The comparison indicates that chloramine usage has increased across the board, regardless of source water type or system size. For background information on UCMR 2, see USEPA (2015c).

Exhibit B.26 shows another important difference between the surveys: hypochlorite use has increased dramatically in the 199 systems between the time of the DBP ICR and the UCMR 3. At the time of the DBP ICR, only 13.0 percent of surface water plants at the common systems employed hypochlorite, presumably bulk hypochlorite solution. (On-site generation of hypochlorite was not common at that time, and it was not tracked as a separate category in the survey.) By the time of UCMR 3, nearly half (42.7 percent) of the surface water facilities at the common systems used hypochlorite in one form or another, and 11 percent were generating hypochlorite on-site.

The foregoing indicates that usage of chlorine dioxide and sodium hypochlorite has increased over the last two decades. This finding is not unexpected. EPA believes the increase has been driven by (a) the need to comply with the Stage 1 and Stage 2 Disinfectants and Disinfection Byproducts Rules and (b) concerns over the safety of storing and transporting gaseous chlorine. In a 2007 American Water Works Association (AWWA) survey, 70 of 233 respondents indicated that they had switched from gaseous chlorine to another disinfectant in the past eight to ten years (AWWA, 2008a, 2008b; see also the preceding survey by AWWA, 2000a, 2000b). Over 80 percent of the systems that had ceased using gaseous chlorine had switched to some form of hypochlorite.

Exhibit B.24: DBP ICR and UCMR 3 Comparison – Use of Disinfectants in Surface Water Plants (Select Categories)

Among 199 Common Systems	Total Number of SW Plants / EPs	Number of Plants / EPs with Exclusive Use of Chlorine (% of Total)	Number of Plants / EPs with Exclusive Use of Chloramines, OR Both Chlorine and Chloramines (% of Total)	Number of Plants / EPs with Any Instance of Chlorine Dioxide (% of Total)	Number of Plants/ EPs with Any Instance of Ozone (% of Total)	Number of Plants / EPs with Any Instance of UV Light (% of Total)	Total Number of SW Plants/ MRs	Number of Plants / MRs with Any Instance of Chloramines (% of Total)
DBP ICR ¹	262	149 (56.9%)	75 (28.6%)	24 (9.2%)	14 (5.3%)	0 (0.0%)	262	113 (43.1%)
UCMR 3 ²	342	137 (40.15%)	101 (29.5%)	44 (12.9%)	50 (14.6%)	17 (5.0%)	238	128 (53.8%)

1. The DBP ICR timeframe was 1/1998 through 12/1998. DBP ICR counts of the number of SW plants were generated as follows: exclusive use of chlorine => plant used no other disinfectant except chlorine (CL₂); exclusive use of chloramines, OR both chlorine and chloramines => plant used no other disinfectant except chloramine (CLM) or chloramine & chlorine (CL₂_CLM); any instance of chlorine dioxide => plant used chlorine dioxide (and may have also used other disinfectants); any instance of ozone => plant used ozone (and may have also used other disinfectants); any instance of UV light => plant used UV (and may have also used other disinfectants); any instance of UV light => plant used UV (and may have also used other disinfectants); To determine the number of plants with any instance of chloramines in MR locations in the DBP ICR, the data field for the disinfectant type in the distribution system was consulted. Only DBP ICR plants served by surface water were included.

2. The UCMR 3 timeframe was 1/2013 through 5/2016. UCMR 3 counts of the number of SW EPs were generated as follows: exclusive use of chlorine => EP used no other disinfectant except chlorine (CLGA, CLOF, or CLON); exclusive use of chlorine, OR both chlorine and chloramines => EP used no other disinfectant except chloramine (CAGC, CAOF, or CAON) or chloramine and chlorine dioxide => EP used chlorine dioxide (and may have also used other disinfectants); any instance of chlorine dioxide => EP used ozone (and may have also used other disinfectants); any instance of ozone => EP used UV (and may have also used other disinfectants); any instance of UV light => EP used UV (and may have also used other disinfectants); any instance of uv light => EP used UV (and may have also used other disinfectants); any instance of uv light => EP used UV (and may have also used other disinfectants); any instance of uv light => EP used UV (and may have also used other disinfectants); any instance of uv light => EP used UV (and may have also used other disinfectants); any instance of uv light => EP used UV (and may have also used other disinfectants); any instance of uv light => EP used UV (and may have also used other disinfectants); any instance of uv light => EP used UV (and may have also used other disinfectants); any instance of uv light => EP used UV (and may have also used other disinfectants); any instance of uv light => EP used UV (and may have also used other disinfectants); any instance of uv light => EP used UV (and may have also used other disinfectants, under the source water designation "SW" were included in this analysis; those served by ground water, ground water under the direct influence of surface water ("GU") or mixed source water ("MX") were excluded.
Exhibit B.25: Comparison of Chloraminating Systems in UCMR 2 and UCMR 3

Data Source	Sampling Location Source Water Type ¹	Number of Sample Locations Using Chloramines at Systems Serving ≤ 100,000 (and Percent of Total) ²	Number of Sample Locations Using Chloramines at Systems Serving > 100,000 (and Percent of Total) ²
UCMR 2 ³	SW	165 (21%)	467 (44%)
UCMR 2 ³	GW	95 (5%)	238 (9%)
UCMR 3 ⁴	SW	1,467 (27%)	472 (48%)
UCMR 3 ⁴	GW	1,247 (8%)	348 (12%)

1. The source water type of the sampling location (listed as "FacilityWaterType" in the UCMR databases) was used to develop these counts. Also, the "SW" category <u>does not include</u> "GU," "MX" or "unknown."

2. A sample location is defined as a unique combination of PWSID / Facility ID / Sample Point ID. Note that this exhibit is presenting information on all chloraminating sample locations in UCMR 2 and UCMR 3, not just those sample locations that are common to both rounds of UCMR.

3. The UCMR 2 timeframe was 2008 through 2011. Counts of the UCMR 2 chloraminating sampling locations were derived using the facility-level disinfection type. All facilities listed as "CA only" or "CA w/ CL-OT" were included in the counts. Under UCMR 2, "CA" stood for chloramination, "CL" stood for chlorination and "OT" stood for other disinfectants (including ozone, chlorine dioxide and UV).

4. The UCMR 3 timeframe was 1/2013 through 5/2016. Counts of the UCMR 3 chloraminating sampling locations were derived using the "UCMR3_DRT" table from the July 2016 version of the database. All facilities listed as having at least one occurrence of "CAGC," "CAOF" or "CAON" were included.

Exhibit B.26: DBP ICR and UCMR 3 Comparison – Hypochlorite Use in Surface Water Plants

Among 199 Common Systems	#Plants / #EP Locations (For SW only) ¹	Number (and Percent) of Plants / EP Locations Using Bulk Solution Hypochlorite (A)	Number (and Percent) of Plants / EP Locations Using On-site Generated Hypochlorite (B)	Number (and Percent) of Plants / EP Locations Using A and/or B
DBP ICR ²	262	34 (13.0%)	N/A	N/A
UCMR 3 ²	342	115 (33.6%)	39 (11.4%)	146 (42.7%)

1. SW counts in this table do not include ground water under the direct influence of surface water (GU) or mixed systems (MX).

2. The DBP ICR timeframe was 1/1998 through 12/1998. For DBP ICR, the counts represent the number of plants. It was assumed that any plants in the TUXHYPO table were using hypochlorite and those not in the table were not using hypochlorite. Since on-site generation was not a common practice at the time of the DBP ICR and was not tracked as a separate category, it is assumed that all hypochlorite was bulk hypochlorite solution.

3. The UCMR 3 timeframe was 1/2013 through 5/2016. For UCMR 3, the counts represent the number of entry points (EPs). "Bulk Hypochlorite Solution (A)" was counted as all EPs with disinfectant types "CAOF" and/or "CLOF". "Onsite Generated Hypochlorite (B)" was counted as all EPs with disinfectant types "CAON" and/or "CLON". In summary: Disinfection techniques have changed over time. A comparison of data from DBP ICR to UCMR 3 suggests that exclusive use of gaseous chlorine diminished, while use of chlorine dioxide, ozone and ultraviolet light increased. Rates of chloramine use as a primary disinfectant have stayed fairly stable, while chloramine use as a secondary disinfectant (to maintain a disinfectant residual in the distribution system) increased. Furthermore, hypochlorite use appeared to have increased dramatically when comparing data from systems in both the DBP ICR and the UCMR 3 data sets. In addition, a comparison of data from UCMR 2 to UCMR 3 suggests a substantial increase of chloramine use. Implications of these observed changes on occurrence of different groups of DBPs are further discussed in EPA's *Six-Year Review 3 Technical Support Document for Disinfectants/Disinfection Byproducts Rules* (USEPA, 2016a).