The Potential Regulatory Implications of Chlorate

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1. Introduction

The purpose of this briefing paper is provide background information on chlorate, as chlorate is currently on the short list of contaminants being considered and evaluated further for the third regulatory determination from the Unites States Environmental Protection Agency's (USEPA's) third contaminant candidate list (CCL3) (Roberson 2012). The CCL3 listed 116 contaminants currently not subject to any national primary drinking water regulation under the Safe Drinking Water Act (SDWA). Used in agriculture and as a bleaching agent in the pulp, paper, and the textile industry, chlorate is also known to occur in drinking water as a result of the disinfection process and as a result of hypochlorite degradation. The occurrence, health effects, analytical methods, and treatment for chlorate are important for the drinking water community to understand prior to a regulatory determination and/or a potential regulation.

At a June 16, 2011 stakeholder meeting, the USEPA summarized occurrence data for 32 of the 116 CCL3 contaminants, including chlorate (Table 1). Most of the national occurrence data used for regulatory determinations comes from prior Unregulated Contaminant Monitoring Rules (UCMRs). Chlorate was included in the earlier Information Collection Rule (ICR) for systems using chlorine dioxide or hypochlorite as a disinfectant. The ICR, however, has limited relevance for the current regulatory development process because the monitoring was conducted in 1997-1998, thereby not accounting for the increase in hypochlorite use since then. Additionally, the ICR only applied to systems serving more than 100,000 people and did not require monitoring for consecutive systems. Chlorate was included in the ongoing third Unregulated Contaminant Rule (UCMR3) monitoring.

Table 1: 32 CCL3 contaminants discussed during June 2011 stakeholder meeting (Roberson 2012)

32/116 CCL3 contaminants	
Nitrosamines	Perfluorooctanic acid (PFOA)
N-nitrosodimethylamine (NDMA)	RDX (cyclotrimethylenetrinitramine)
N-nitrosodiethylamine (NDEA)	Dimethoate
N-nitrosodi-n-propylamine (NDPA)	Disulfoton
N-nitrosopyrrolidine (NPYR)	Diuron
N-nitrosodiphenylamine (NDPhA)	Molinate
Chlorate	Terbufos
Molybdenum, Strontium, & Vanadium	Terbufos sulfone
1,1,2-Tetrachloroethane	Acetochlor
1,2,3-Trichloropropane (TCP)	Actochlor ethanesulfonic acid
1,3-Dinitrobenzene	Acetochlor oxanilic acid
1,4-Dioxane	Alachlor ethanesulfonic acid
Methyl *tert* butyl ether (MTBE)	Alachlor oxanilic acid
Nitrobenzene	Metolachlor
Perfluorooctane sulfonic acid (PFOS)	Metolachlor ethanesulfonic acid
	Metolachlor oxanilic acid

As part of the regulatory development process, health effect data are assessed in developing a health reference level (HRL) to provide a benchmark for the occurrence data. National occurrence data compared to the HRL is summarized in Table 2.

Table 2: Summary of chlorate occurrence data (adapted from Roberson 2012)

Contaminant	**HRL µg/L**	**Occurrence Data Source**	**Systems or samples with detects (>HRL, %)**
Chlorate*	210	ICR hypochlorite	22/59 (37)
		ICR chlorine dioxide	15/29 (52)

*Included in UCMR3

1.1 Physiochemical properties

Chlorate often persists in the environment and drinking water as a product from chlorine, chlorine dioxide, and chlorite chemical reactions in an aqueous environment; therefore, the physiochemical properties of sodium chlorate and other chlorine-based disinfectants used in drinking water treatment are tabulated in Table 3.

Table 3: Physiochemical properties of chlorine, chlorine dioxide, sodium chlorite, and sodium chlorate (NAS 1987; The Merck Index 2006)

Property	Chlorine	Chlorine Dioxide	Sodium Chlorite	Sodium Chlorate
Molecular formula	Cl_2	ClO_2	$NaClO_2$	$NaClO_3$
CAS Number	7782-50-5	10049-04-4	7758-19-2	7775-09-9
Oxidation state of Chlorine	0	+4	+3	+5
Melting point	-102 °C	-59 °C	180-200 °C (anhydrous, decomposition)	248 °C
Boiling point	-35 °C	10 °C	N/A	~300 °C (decomposition)
Water solubility (g/L)	6 (25°C)	3.01 (25°C)	390	1000
Properties at room temperature	Greenish-yellow gas	Reddish-yellow gas	Hygroscopic crystal/flake, white solid	Colorless, odorless crystals or white granules

1.2 General uses and environmental exposure

Aqueous chemical reactions and the handling of chemicals used in drinking water treatment is the dominant source of environmental exposure to chlorate. Even though chlorine and chlorine dioxide are commonly used in drinking water disinfection, all four chemical substances listed in Table 3 may potentially persist in finished water. Exposure from other drinking water treatment processes include formation of chlorate during the on-site preparation of chlorine dioxide using sodium chlorite and during the onsite generation of hypochlorite or the storage of bulk hypochlorite; therefore, chlorine, chlorine dioxide, and chlorite are considered with chlorate chemistry in the following sections.

Outside of exposure from drinking water treatment processes, the industrial uses of chlorate can lead to unsafe levels persisting in the environment. All four chlorine substances presented in Table 3 are used in the pulp, paper, and the textile industry as bleaching agents. Additionally, chlorine dioxide is used in the leather tanning industry. Chlorate is also introduced to the environment as an herbicide and as through its use as a pharmaceutic aid (The Merck Index 2006). Chlorine dioxide, chlorite, and chlorate can occur in foods as they are used in flour processing, as decolorizing agents, as bleaching agents, and as an indirect additive from paper packaging. According to the Food and Drug Administration (FDA), chlorine dioxide is also considered a food contact substance (FCS) and, in sodium chlorite-based systems, is used for antimicrobial applications in poultry, fruit, and vegetable processing (Borodinsky 2011).

The sections that follow review the occurrence of chlorate in drinking water from drinking water treatment processes and briefly review agricultural and industrial exposure to chlorate. Health effects, an assessment of both analytical and treatment methods, along with a brief review of the other

regulatory actions concerning chlorate are also part this briefing paper. This paper is intended to provide an overview of available information on chlorate and to provide more information for the drinking water community prior to regulatory decisions being made concerning chlorate in drinking water.

2. Occurrence

2.1 Chemical Occurrence at Treatment Plants

When chlorine dioxide is used as a disinfectant, it acts as a strong oxidant. After application, chlorite is the dominant species in drinking water through one electron transfer during oxidation.

$ClO_{2\,(aq)} + e^- = ClO_2^-$ (E^o=0.954V) Equation 1

Production of chlorine dioxide for drinking water treatment can be generated by several onsite methods including the reaction of sodium chlorite with gaseous chlorine, hypochlorous acid, or hydrochloric acid through the following reactions (Equation 2a-c) (USEPA 815-R-99-014 1999).

$2NaClO_2 + Cl_{2(g)} = 2ClO_{2\,(g)} + 2NaCl$ Equation 2a

$2NaClO_2 + HOCl = 2ClO_{2\,(g)} + NaCl + NaOH$ Equation 2b

$5NaClO_2 + 4HCl = 4ClO_{2\,(g)} + 5NaCl + 2H_2O$ Equation 2c

Chlorate is often an undesirable byproduct of this process. An intermediate dimer, $\{Cl_2O_2\}$, occurs rather than chlorite being completely converted to chlorine dioxide. This unstable, asymmetrical intermediate can lead to the formation of chlorate when the process is reactant limited as shown in equations 3a-c (Singer and O'Neil 1987; USEPA 815-R-99-014 1999).

$\{Cl_2O_2\} + H_2O = ClO_3^- + Cl^- + 2H^+$ Equation 3a

$\{Cl_2O_2\} + HOCl = ClO_3^- + Cl^- + H^+$ Equation 3b

$\{Cl_2O_2\} + 3HOCl + H_2O = 2ClO_3^- + 5H^+ + 3Cl^-$ Equation 3c

Several conditions can lead to the production of chlorate at drinking water facilities. In the above reactions, the creation of chlorate during the chlorine dioxide generation occurs during low chlorite concentrations and at low pH. Acidic mixtures, in general, are more likely to favor the production of chlorate over chlorite during chlorine dioxide generation. Chlorate and chlorite ions can also occur as photodecomposition byproducts of chlorine dioxide (Bolyard et al. 1993). Furthermore, when chlorine is added in the presence of residual chlorite as a secondary disinfectant, the chlorite can

undergo oxidation to chlorate (Singer and O'Neil 1987).

Concentrations of chlorate within the distribution system can also vary by sampling point (distance within the system) and time of year. A study reported in the Canadian Federal-Provincial-Territorial Committee on Drinking Water (CDW) measured chlorine dioxide, chlorite, and chlorate after treatment (T) and throughout a distribution system (D1, D2, D3) of a utility using chlorine dioxide disinfection. The study tracked the concentrations during winter months and summer months (Health Canada 2005). The results presented in Table 4 report the maximum chlorate concentrations measured in Canada during the summer as higher than during the winter and were relatively constant throughout the system.

Table 4: Concentrations of measured chlorine dioxide, chlorite ion, and chlorate ion in Quebec distribution systems (adapted from Health Canada 2005)

Chemical	Season	T	D1	D2	D3
Chlorine dioxide (mg/L)	Winter	0.01-0.53 (avg. 0.22)	<0.01-0.21 (avg. 0.09)	<0.01-0.22 (avg. 0.09)	<0.01-0.06 (avg. 0.03)
	Summer	<0.01-0.63 (avg. 0.32)	Not analyzed	Not analyzed	Not analyzed
Chlorite ion (mg/L)	Winter	<0.026-0.872 (avg. 0.36)	<0.026-0.846 (0.36)	<0.026-0.769 (0.34)	<0.026-0.686 (0.29)
	Summer	<0.033-1.617 (avg. 0.48)	<0.033-1.557 (avg. 0.45)	<0.033-1.58 (avg. 0.44)	<0.033-1.253 (avg. 0.39)
Chlorate ion (mg/L)	Winter	<0.032-0.308 (avg. 0.13)	<0.032-0.321 (avg. 0.13)	<0.032-0.289 (avg. 0.12)	<0.032-0.308 (avg. 0.13)
	Summer	0.081-0.586 (avg. 0.21)	0.115-0.611 (avg. 0.22)	0.112-0.592 (avg. 0.22)	0.151-0.576 (avg. 0.22)

Aside from chlorine dioxide systems, another important source of chlorate ions in drinking water is from the manufacturing and storage of hypochlorite solutions (Bolyard et al. 1993; EPA 815-R-99-014 1999). Hypochlorite is unstable with respect to disproportionation. Heat and basic solutions lead to the favorable disproportionation reaction below (equilibrium constant, K, of 10^{27}) and can lead to considerable chlorate in the hypochlorite stock during storage (Equation 4).

$$3ClO^- = 2Cl^- + ClO_3^-$$ Equation 4

In a study surveying 11 utilities (15 sites) using hypochlorite as a source of chlorine for disinfection, the chlorate concentration in stock hypochlorite solutions was correlated to the chlorate concentration in finished water (Boylard et al. 1993). A selected number of sites are summarized in Table 5 below. This study concluded that there is a correlation between the free available chlorine (FAC) concentration and the concentration of chlorate. A lack of monitoring of the FAC concentration in the stock hypochlorite over time led some utilities to be unaware of hypochlorite deterioration and increasing concentrations of chlorate in the stored supply.

Table 5: Degradation of hypochlorite solutions used for disinfection (from Bolyard et al. 1993)

Form of Hypochlorite Solution	FAC concentration in hypochlorite solution (from supplier) (g/L)	Actual FAC concentration in hypochlorite solution (measured by USEPA) (g/L)	Normalized ClO_3^- in hypochlorite solution (µg ClO_3^-/mg FAC)
5% NaOCl	50	60	17
10% NaOCl	100	110	72
13-15% NaOCl	130-150	110	100
13-15% NaOCl	130-150	110	100
11% NaOCl	110	100	150
15% NaOCl	150	100	190
11% NaOCl	110	86	209
15%NaOCl*	150	19	2,200

*This site was for a low-production well and stored the hypochlorite on site longer than any of the other utilities surveyed.

Since the Boylard et al. study in 1993, more research occurred to better understand chlorate resulting from hypochlorite storage and to communicate the importance of proper storage and handling to utilities. Stanford et al. (2011) noticed the same degradation of hypochlorite in stock solution with time as Boylard et al. (1993) but included a variety of hypochlorite production and storage variables from seven utilities. Table 6 tabulates the chlorate as measured in the hypochlorite, raw water, and finished water for the seven utilities using either bulk or on-site generation of hypochlorite.

Table 6: Summary of chlorate concentrations in raw water, finished water, and hypochlorite used at participating utility locations (Stanford et al. 2011)

Utility	Source	FAC (g/L)	ClO_3^- Hypo (mg/L)	ClO_3^- Raw (mg/L)	ClO_3^- Fin. (mg/L)	Mass ClO_3^- per mg FAC (µg/mg FAC)
UTL1-A	Bulk	87	19,000	0.014	0.58	220
UTL1-B	OSG 9	6.8	480	0.026	1.5	110
UTL 2	Bulk	150	5,900	0.005	0.019	39
UTL 3	Cl_2 Gas	n/a	n/a	<0.003	<0.003	n/a
UTL 4	Bulk	120	1,800	0.13	0.20	15
UTL 5	OSG 10	8.7	380	0.008	0.16	90
UTL 6	Bulk	120	2,400	<0.003	0.13	20
UTL 7	Bulk	130	8,000	<0.003	0.79	62

Hypo = Hypochlorite solution; Raw = Raw water entering the treatment plant; Fin = Finished water leaving treatment plant; Samples analyzed in duplicate measurements, with average % difference for ClO3- 2.5%

The results from this study make it very apparent that for these utilities, all the chlorate concentrations in the finished water were a result of water treatment. Work by Stanford et al. (2011) determined that control of chlorate in bulk hypochlorite solutions can be easily achieved by dilution of the delivered hypochlorite solution using softened water or by cooling the solution. Regardless of the method of hypochlorite application, a notable conclusion was that as the FAC in the hypochlorite solution decreased, operators were forced to feed in more hypochlorite to achieve target chlorine doses for treatment thereby increasing the chlorate dose over time as well.

In a subsequent study, Stanford et al. (2013) investigated the temporal variability of chlorate at low-strength onsite-generation facilities. There was considerable variation between onsite-generation units, even with replicate tests. One example provided in the article discussed the standard deviation of eight generators at a single facility as ± 173,000 µg/L, translating to a possible chlorate dose from 75-275 µg/L in the finished water (assuming an FAC use level of 5 mg/L). The ability to control this variability within a single facility is difficult and the observed variability could potentially be greater if more utilities were reviewed with the same detail as the Stanford et al. (2013) study.

The American Water Works Association (AWWA) released a "Hypochlorite Assessment Model" tool in early 2012 to help utilities predict expected levels of chlorate in stored bulk hypochlorite solutions. The predictions are based on inputs from operators that included initial hypochlorite conditions, storage temperatures, pH, and initial concentrations of other ions (if available). The model can be run with as little user-supplied information as the concentration of the hypochlorite solution,

temperature, and holding time (in days) (AWWA 2012).

2.2 ICR Database

Nationally, the most comprehensive set of results for chlorate is contained in the Information Collection Rule (ICR) database (EPA 2011). The ICR database was collected through monitoring conducted over 18 months from July 1997 to December 1998. The database is a collection of occurrence and treatment information for very large systems (serving at least 100,000 people). In total, 296 public water systems (PWS) gathered information pertaining to water quality, microbial contamination, disinfection by-products (DBPs) occurrence and precursors, and treatment plant designs and operating parameters as required by the ICR. Systems serving ≥ 100,000 people conducted all of the monitoring while only certain groundwater systems monitored beyond treatment designs and operations (McGuire et al. 2002). All systems using chlorine dioxide or hypochlorite were required to measure chlorate at the treatment plant influent and effluent with chlorine dioxide plants required to measure monthly and hypochlorite plants quarterly. This represents 82 utilities from the database of systems (28%) and includes 1558 influent and finished water samples for chlorate. This database is unique in that it includes long term monitoring (over a total of 18 months) for chlorate, whereas most monitoring programs are for a shorter period of time. The minimum reporting limit for chlorate in this study was 20 µg/L.

Approximately 49% of all the ICR influent and finished water results were non-detects. Many of the non-detects (623 samples) contained within the system were measurements of chlorate in the plant influent (raw water). There were situations where influent measurements were considerably high as well. To simplify the analysis for this briefing paper, only the finished water samples for chlorate were used in the following discussion. Limiting the database to only finished water, the list of PWS reporting chlorate measurements for some or all of the 18 monitoring months was reduced to 74 systems and, when cross compared with the SDWIS database, 70 systems contained geographic information. For the purpose of this briefing paper, two systems in Utah without direct references in the SDWIS database were assumed to be geographically located in Salt Lake City. The 95th percentile value associated with each PWS was used in the analysis of chlorate concentrations entering distribution systems. Figure 1 shows the distribution of available data and measured chlorate concentrations in finished water regardless of disinfection method used.

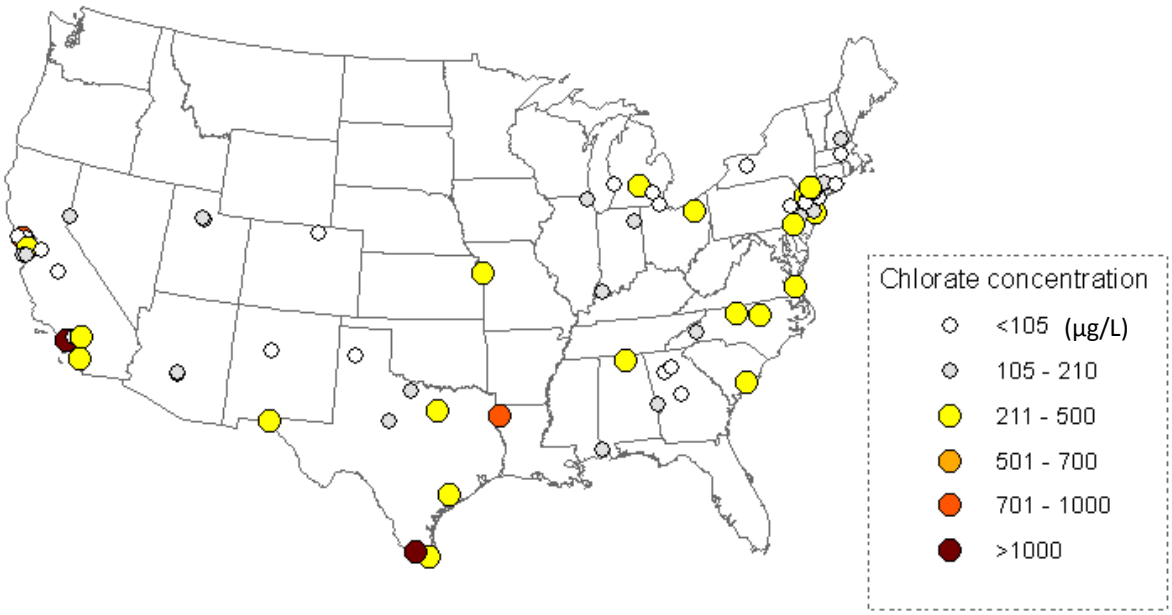


Figure 1: Map of sampled and observed 95th percentile chlorate levels in finished water (ICR database)

The USEPA has calculated a Health Reference Level (HRL) for chlorate of 210 µg/L. Within the ICR database, 16% of all finished water samples collected are greater than the HRL. Once the 95th percentile was calculated and associated with the 74 PWS reporting finished water chlorate concentrations, 26 of these systems (35%) contain values greater than the HRL. The limited number of PWSs makes it difficult to assess any geographic trends in Figure 1.

The ICR primary (AUX1) database also contains disinfection records for surface water treatment plants during the last 12 months of ICR monitoring (McGuire et al. 2002). Cross referencing the type of treatment with residual chlorate concentrations in finished water, Figure 2 shows only the systems using chlorine dioxide (Figure 2a) or hypochlorite (Figure 2b) as a disinfectant at the treatment plant (not the distribution system disinfection). While the database contains information on chlorine dioxide, chlorine did not distinguish between chlorine disinfection types and is labeled simply as "chlorine disinfection" in the database; however, it is possible to extract information on measurements from the stock hypochlorite solutions (TUXHYPO table). Cross referencing the treatment plant ID with PWSID's, the utilities using hypochlorite were determined. The majority of the systems contained chlorate values less than the HRL with 36% of the chlorine dioxide systems and 31% of the hypochlorite systems exceeding this health reference level. The limited number of treatment plants reporting monitoring concentrations for chlorate complicates any occurrence analysis or any national extrapolation for chlorate.

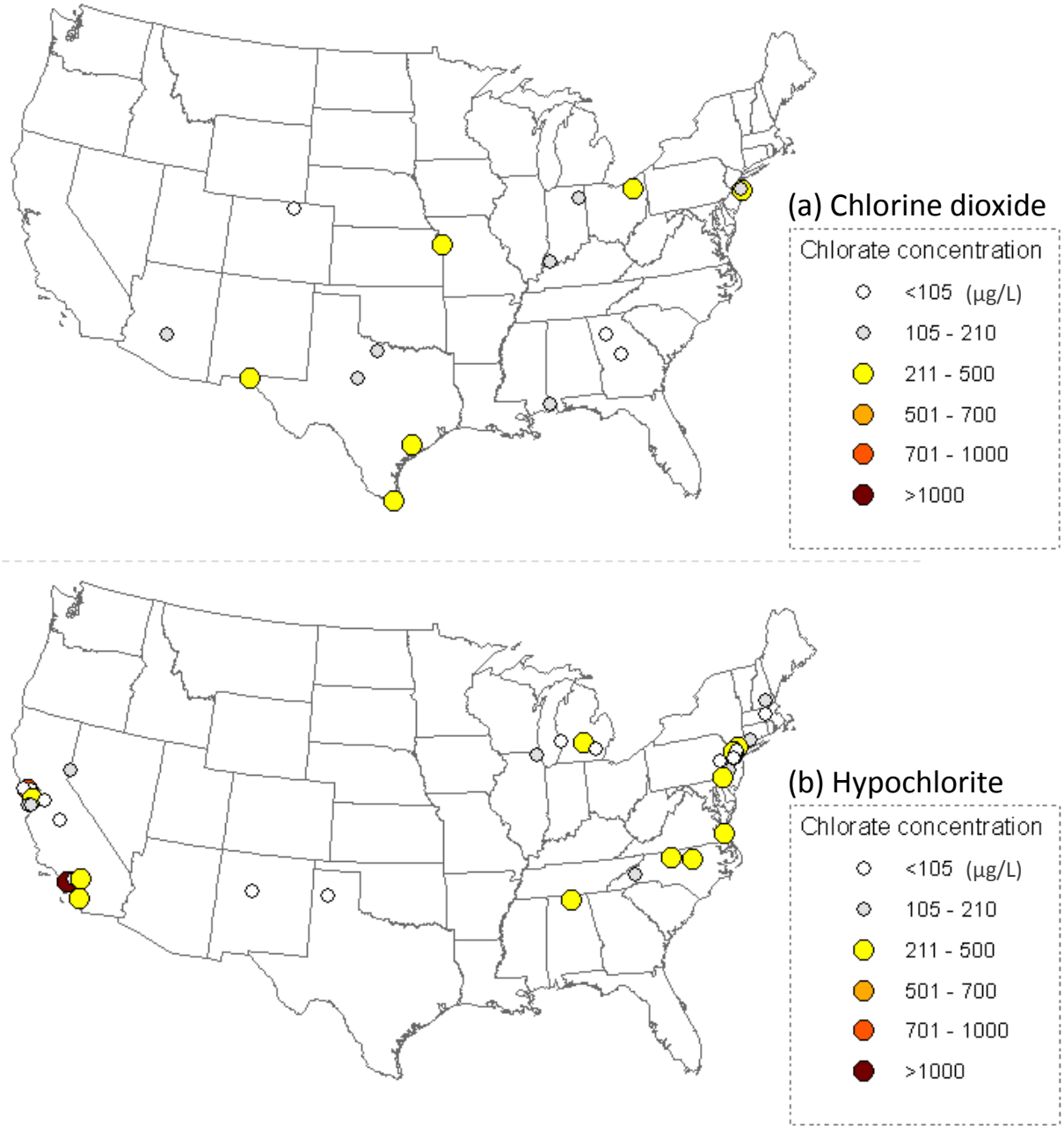


Figure 2: Map of sampled and observed chlorate in finished water using (a) chlorine dioxide disinfection and (b) hypochlorite as a disinfectant. (ICR database)

The ICR database also allows for temporal comparisons within systems since chlorine dioxide systems were required to collect samples every month for the entire 18 month period. Selecting four PWSs measuring chlorate for the duration of the study using chlorine dioxide treatment at the plant, Figure 3 contains four plots, one for each PWS, of chlorate concentrations over time. Two facilities selected, from NJ and KS, reported duplicate samples for quality control. Little variation exists in the KS

and GA utilities from month to month and between replicates for the KS facility. The NJ and OH facilities show greater variation. Except for KS, the facilities included in Figure 3 dose with free chlorine prior to distribution. The large variance in the plots demonstrates the necessity to understand more regarding the onsite generation and treatment to draw conclusions on chlorate concentrations related to chlorine dioxide disinfection.

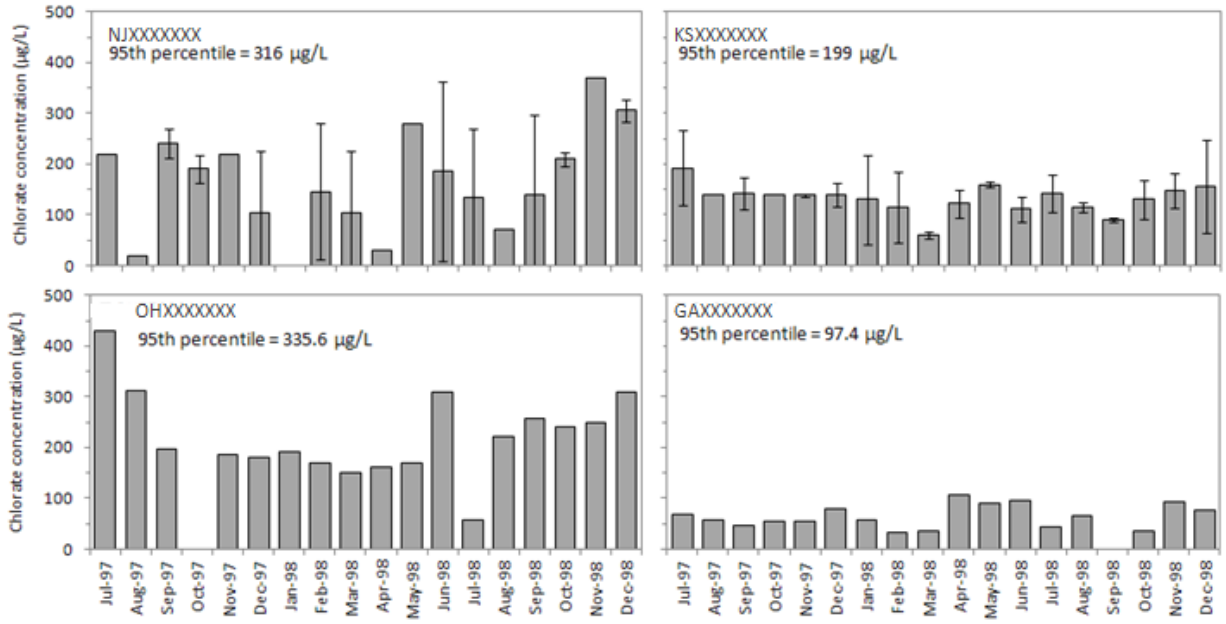


Figure 3: Seasonal variation of chlorate measurements for selected PWS practicing chlorine dioxide disinfection at the treatment plant.

The ICR database also provided sampling information regarding the hypochlorite stock solutions. Using the ICR data, the stock hypochlorite chlorate concentrations, FAC concentrations, pH, and hypochlorite temperature can all undergo comparison. Normalizing the chlorate concentrations in the hypochlorite stock by the corresponding FAC concentrations, the impact of the stored hypochlorite temperature on the chlorate/FAC concentration ratio is directly compared in Figure 4 and displays a slightly increasing trend in chlorate concentrations as hypochlorite temperature increases. The temperature dependence exhibited in Figure 4 is consistent with the trends reported by Stanford et al. (2011) and the requirement by the AWWA Hypochlorite Tool for storage temperature in order to predict the FAC of the bulk hypochlorite solution. The limitation to these comparisons is the unknown age of the hypochlorite stock.

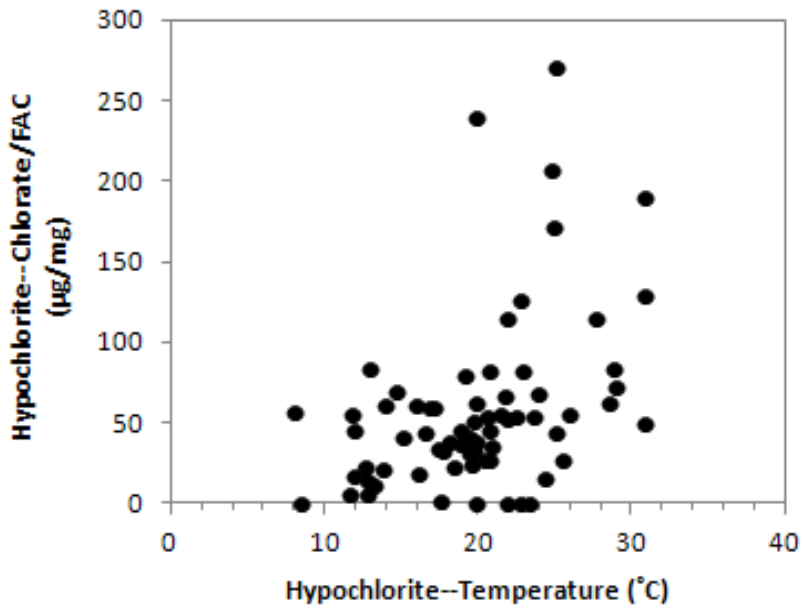


Figure 4: Stock hypochlorite temperature related to chlorate/FAC ratios. Data from several different PWS's and all sampling periods are displayed without identification to observe overall trends at utilities.

Expanding the analysis of hypochlorite stock further, the hypochlorite chlorate versus FAC concentrations are plotted in Figure 5. The scatter of data in Figure 5 does not display any trend relating decreasing FAC concentrations to increasing chlorate concentrations in the hypochlorite stock. The lack of any discernible trend indicates that many factors (i.e. temperature, storage age, original FAC concentration, etc.) are important factors and a direct correlation is not always possible. Furthering the analysis, Figure 6 compares chlorate/FAC concentration ratios in the stock hypochlorite to finished water chlorate concentrations. This could not be queried directly in the AUX1 database, but was achieved by first extracting the hypochlorite stock data by PWSID and sampling period into a separate table within the database and cross-referencing with finished water chlorate values for each PWS and sampling period available. While there is not a strong trend exhibited in Figure 6, a slight increasing trend for half the data correlates increasing chlorate in finished water with increasing chlorate in the hypochlorite stock. Limiting this analysis is, again, the age of the hypochlorite stock along with the original FAC concentration to relate decreasing FAC concentrations in the hypochlorite stock with increasing chlorate concentrations in the finished water.

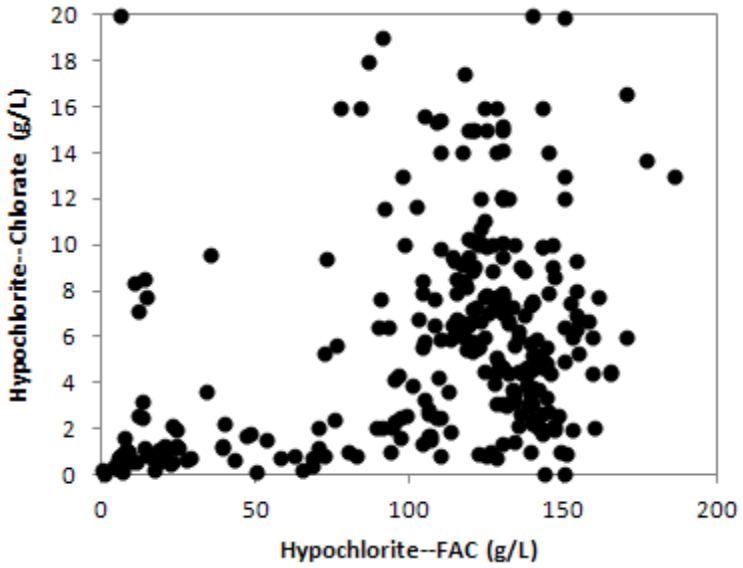


Figure 5: Stock hypochlorite chlorate and FAC concentrations. Data from several different PWS's and all sampling periods are displayed without identification to observe overall trends at utilities.

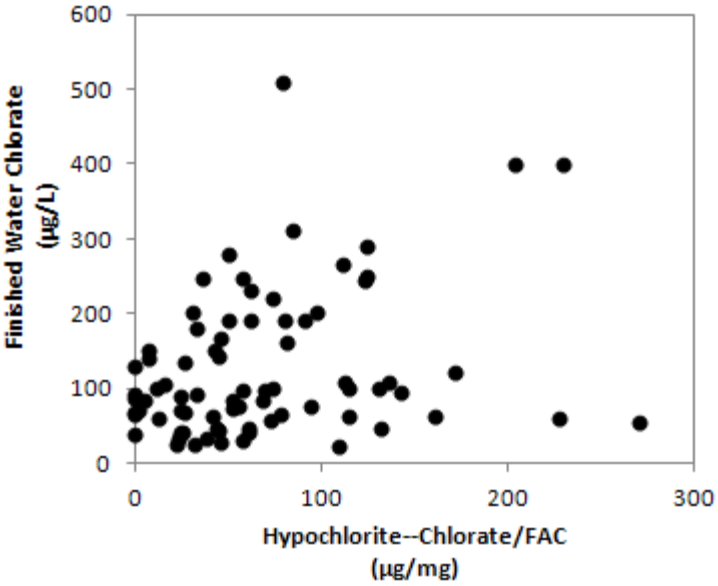


Figure 6: Relationship between concentrations of chlorate in finished water and in stock hypochlorite solutions. Data from several different PWS's and all sampling periods are displayed without identification to observe overall trends at utilities.

For the past 15 years, water treatment plants have seen a gradual shift from gaseous chlorination to hypochlorination starting with the regulatory requirements for risk management plans in Section 112(r) of the Clean Air Act. The ICR database was conducted early in this shift and, therefore, does not capture the increasing prevalence of hypochlorination in new and/or renovated water treatment plants. In a 2007 disinfectant-specific survey, chlorine gas remained the most prevalent

disinfectant used; however, 25% of those surveyed plan to switch to hypochlorite (either bulk or on site generation) in the future (AWWA Disinfection Systems Committee 2008a and 2008b).

2.3 Agricultural Uses and Occurrence: Pesticides, Herbicides, Defoliants

The Midwest and South Central regions are areas of high meat processing, farming, and food processing where chlorate substances are used in the processing and farming industries. For this reason, this section evaluates the agricultural uses of chlorate and the persistence of this ion in the environment to provide a more holistic view of chlorate persistence in the United States. Data presented in this section also indicate an increased potential for raw water chlorate contamination from agricultural uses in certain areas of the country.

The EPA has published a comprehensive report on the presence of inorganic chlorate in the environment (EPA 2006) as part of the inorganic chlorate reregistration eligibility decision. Sodium chlorate, calcium chlorate, potassium chlorate, and magnesium chlorate are all listed as active ingredients on a variety of products, yet only sodium chlorate was the focus of the reregistration decision. Some products containing sodium chlorate include Atlacide, Defol, De-Folate, Drop-Leaf, Fall, Harvest-Aid, Kusatol, Leafex, and Tumbleleaf (PIP 1995). Sodium chlorate does not exist alone in the herbicide mixtures, and often is mixed with atrazine and other herbicides and fungicides.

Sodium chlorate is applied post-emergence as a pesticide targeting broadleaf weeds. It is a non-selective herbicide that, on contact, penetrates the plant cuticle and disrupts metabolic processes of the plant cells; therefore, it is phytotoxic to all green plant parts (PIP 1995). Agriculturally, sodium chlorate is primarily used in the southern U.S. on cotton; however, it is also applied to a variety of other crops including (but not limited to) rice, corn, soybeans, dry beans, potatoes, sunflowers, flax, safflower, grain sorghum, and wheat in application doses that range from 4-12.5 lbs. a.i./Acre (USEPA 2005). From mapping select crop production in Figure 7a-d, it is apparent that the Midwestern and the Southern United States are the primary locations of crops potentially receiving sodium chlorate applications.

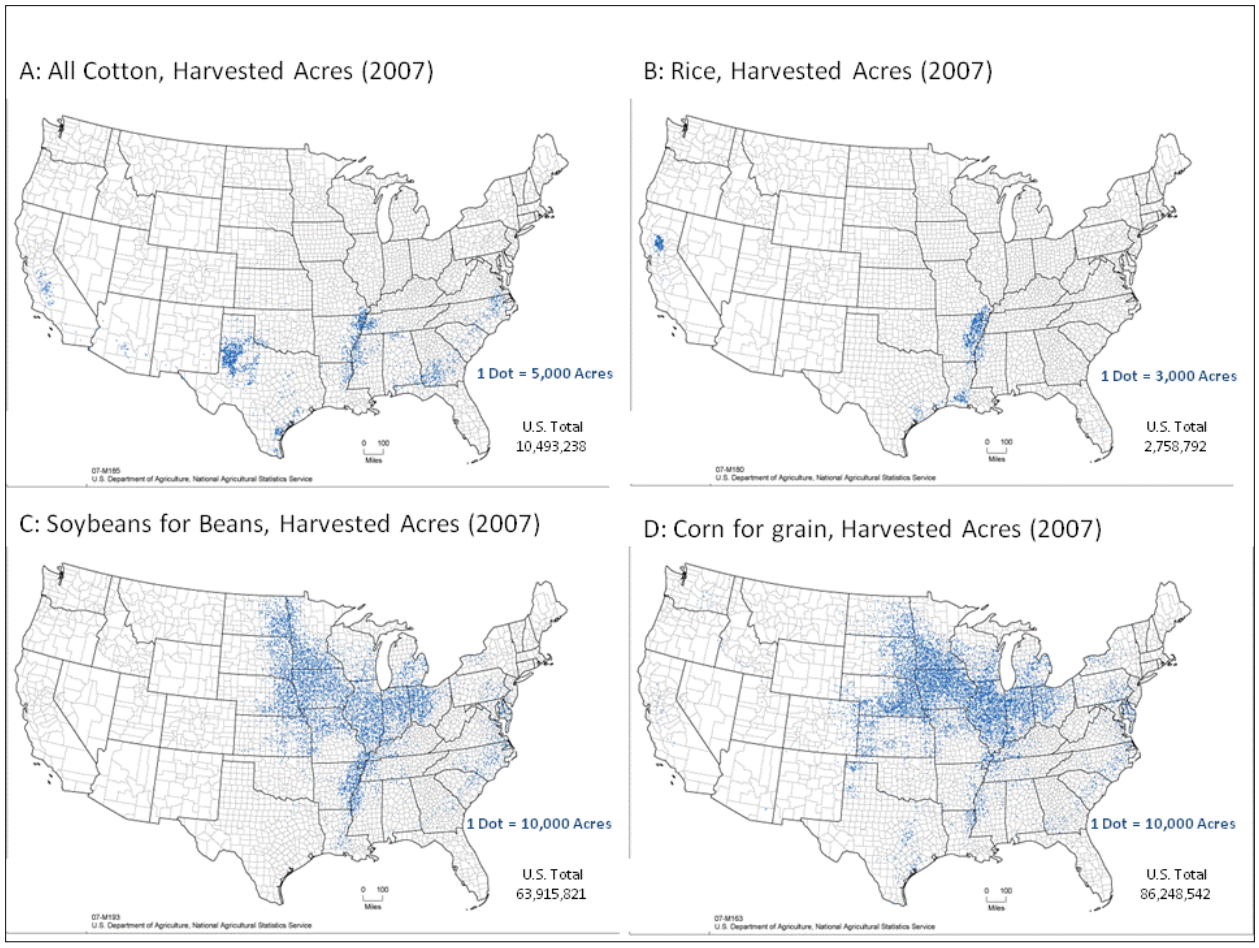
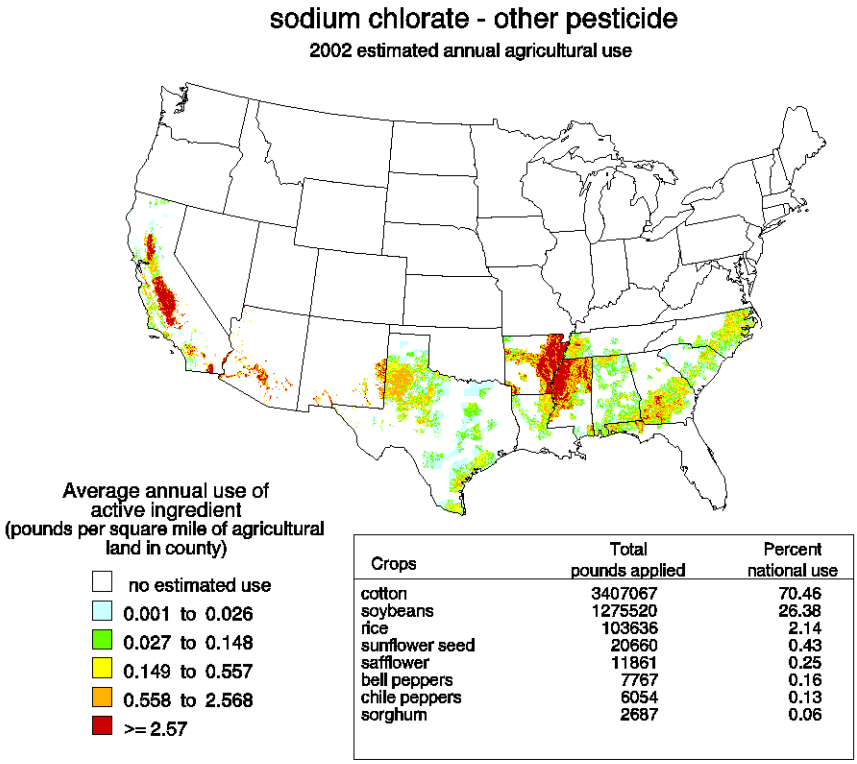


Figure 7: Harvested acres for select crops in the United States during 2007 (adapted from USDA Statistical Data 2007)

The USGS performed a study from 1999 through 2004 to estimate typical pesticide use patterns over a five year period. Figure 8 below is the map of average annual sodium chlorate use expressed as average weight (in pounds) of sodium chlorate applied to each square mile of agricultural land in a county.



Crops	Total pounds applied	Percent national use
cotton	3407067	70.46
soybeans	1275520	26.38
rice	103636	2.14
sunflower seed	20660	0.43
safflower	11861	0.25
bell peppers	7767	0.16
chile peppers	6054	0.13
sorghum	2687	0.06

Figure 8: Estimated sodium chlorate agricultural use in the United States (from USDA water.usgs.gov/nawqa/pnsp/usage/maps)

Non-agricultural uses (residential and industrial) are typically more concentrated applications (620 lbs. a.i./Acre) and include rights-of-way, building perimeters, cracks between concrete, tennis courts, ditch banks, and as a pre-paving treatment (USEPA 2006). Pesticide uses of sodium chlorate (including agricultural applications) account for only approximately 2% of total sodium chlorate used in the United States. This is equivalent to approximately 2.8 million pounds per year applied to agricultural, residential, and commercial sites. Of that, 2.1 million pounds are used on agricultural sites (USEPA 2006). In Arizona alone, 68,126 acres received a total of 332,377 lbs. of sodium chlorate in 2001 (USDA 2001).

When added to water or moist soil, chlorate is fully ionized and is expected to immediately dissociate. The high solubility of chlorate in water does not suggest volatilization from soil and water as a likely transportation route. Chlorate is weakly soluble in n-octanol (<1g/L, P_{ow}<0.001, log P_{ow}<-2.9) (Arkema 2010) and, therefore, is not expected to bioaccumulate in fish.

The chlorate ion is not likely to adsorb to soil/sediment particulates and, therefore, has a high leaching and run-off potential. The run-off potential is greatest immediately after application when a heavy rainstorm could wash chlorate off application sites and concentrate it in streams and waterways (USEPA 2005). During these types of run-off events, agricultural applications could impact drinking water sources. The persistence of chlorate also depends on the levels of oxygen and oxidation-

reduction potential of the environment. Chlorate will persist in waters with a high pE (oxidizing environment). Similarly, chlorate is more stable in acidic than alkaline waters. Seasonal and geographic variabilities are important when considering application and runoff of chlorate from fields.

Based on thermodynamic equilibrium alone, chlorate's end product is chloride; but the rate of reaction and conversion in the natural environment is difficult to estimate (USEPA 2005). An important contribution to the chemical analysis of chlorate in the environment is the redox conditions of the media (soil), concentration of reductants, chlorate concentrations, temperature, pH, and moisture levels of the soil (USEPA 2006). Nitrate concentrations in soil and water are also important when considering the redox potential of an environment. Nitrogen runoff has greatly attributed to dead-zones (hypoxic, low-oxygen areas) along the water of the East Coast of the United States and in the Gulf of Mexico due to denitrification. As the oxygen levels in an environment change, the fate and persistence of chlorate will also vary.

2.4 Ongoing UCMR3 monitoring

The ongoing UCMR3 monitoring will provide a larger database to assist in the national occurrence of chlorate. Early UCMR3 data from USEPA's first public release was compiled in Table 7 for approximately 1000 reporting utilities, resulting in ~6600 samples (USEPA, 2013). The data, thus far, indicates that over 10% of the samples are greater than the USEPA HRL concentration of 210 µg/L and more than 30% of utilities have had a value exceeding the HRL.

Table 7: Preliminary chlorate UCMR3 monitoring results--6561 samples from approximately 600 utilities (USEPA, 2013)

Sample Statistic	Chlorate concentration (µg/L)
95th percentile	360
75th percentile	120
50th percentile	34
Maximum	6200

3. Health Effects

Chlorate is principally toxic by ingestion and inhalation. An oral lethal dose is estimated to be as low as 20 g sodium chlorate (or 230 mg chlorate/kg body weight) (NAS 1980). The use of chlorate in weed killers in the United States has led to many case reports of chlorate intoxication. When ingested, chlorate is absorbed by the gastrointestinal tract and is eliminated by the kidneys, unchanged by processes within the body. Ingestion of high concentrations of chlorate and chlorite produce

methemoglobin and a decreased thyroid function (but is not confirmed by many studies; further research is needed) (NAS 1987). Potassium chlorate can have cumulative toxic effects because it is more slowly excreted from the body.

High levels of chlorate impair the blood's ability to carry oxygen and the toxic effects are derived from chlorate rupturing red blood cell membranes. The rupturing of red blood cells is followed by the formation of methemoglobin by oxidation of free hemoglobin in the blood and is irreversible. In most of the reported cases of chlorate poisoning, a drop in hemoglobin levels were observed with methemoglobin as an early sign of intoxication (NAS 1987).

The most comprehensive study of the effects of chlorate in drinking water was conducted by Lubbers et al. (1981). Single doses of 0.01, 0.1, 0.5, 1.0, 1.8, and 2.4 mg of chlorate ion were ingested in 1 L of drinking water by ten male volunteers per dose (60 volunteers total). Lubbers et al. (1981) also had volunteers consume chlorate at 36 µg/kg/day over a 12 week period and observed them for an additional 8 weeks. Despite this intensive study the authors could not conclude any definitive detrimental physiological impact. Therefore, the highest dose of 2.4 mg/L of chlorate results in a No Observed Effects Level (NOEL) of 36 µg/kg/day.

To calculate a reference dose (RfD) from an experimental study from which a NOEL, NOAEL, BMD, or LOAEL were derived, variations on Equation 5 are used. EPA uses the RfD to establish the maximum contaminant limit goal (MCLG) (EPA 822-R-03-008 2003).

$$\mathrm{RfD} = \frac{\text{BMD or LOAEL or NOAEL}}{\mathrm{UF} \cdot \mathrm{MF}} \qquad \text{Equation 5}$$

where:

NOAEL	=	no- or low-observed-adverse-effect level (mg/kg/day)
LOAEL	=	lowest-observed-adverse-effect level (mg/kg/day)
BMD	=	benchmark dose (mg/kg/day)
UF	=	uncertainty factor
MF	=	modifying factor

The MCLG is then calculated from the RfD according to Equation 6.

$$\mathrm{MCLG}\left(\frac{\mathrm{mg}}{\mathrm{L}}\right) = \frac{\mathrm{Rfd} \cdot \mathrm{BW} \cdot \mathrm{RSC}}{\mathrm{I}} \qquad \text{Equation 6}$$

where:

RfD	=	Reference Dose
BW	=	body weight (70 kg adults, 10 kg children, 4 kg infants)
RSC	=	Relative source contribution (fraction of RfD from drinking water)
I	=	daily intake of drinking water (2 liters for adults, 1 liter for children, 0.64 liter for infants)

According to the UCMR 3 Fact Sheet, the RfD for chlorate is set to 0.03 mg/kg/day and is associated with enlarged thyroid and mineralization (USEPA 2012) concluded from a study in 2004 using

rats. Using this reference dose, the health reference calculations use the assumptions of a 70 kg adult consuming 2 L/d and the default Relative Source Contribution (RSC) of 20% to determine a Health Reference Level (HRL) of 210 µg/L; however, there are multiple other studies available and a range of RSCs to consider. Table 8 calculates the RfD from the experimentally derived adverse levels from three different studies, including the NTP 2004 study used by EPA to calculate their MCLG. Using this RfD, two MCLGs are calculated for each study using either a 20% contribution or 80% Relative Source Contribution (RSC) from drinking water. The EPA default value of 20% RSC was used in their calculation; however, the major source contribution is from drinking water. The McCauley et al. (1995) study is attributed an UF of 1000 (10 each for interspecies, intraspecies, and short duration) in Table 8. Lubbers et al. (1981) did not observe any definitive impacts from their study and, therefore, a default value of 2.4 mg/L is used to calculate the associated RfD in Table 8 even though higher doses are likely applicable.

Table 8: Calculated MCLG and RfD values for chlorate from three different studies

	(NTP 2004)		(Lubbers et al. 1981)		(McCauley et al. 1995)	
MCLG (mg/L)	0.21	0.84	0.084	0.336	0.21	0.84
RfD (mg/kg/day)	0.030		0.011		0.300	
BW (kg)	70		70		70	
RSC	0.2	0.8	0.2	0.8	0.2	0.8
I (L)	2		2		2	
LOEL, NOEL, LOAEL, NOAEL, BMDL (mg/kg/day)	0.9*		0.036		30	
UF	30		3		1000	
MF	1		1		1	

*LOAEL 5 mg/kg/day; BMDL of 28 mg/L

The variability in the calculated values in Table 8 depends on the RSC and the UF attributed to using laboratory studies to determine dose levels for the entire human population. These three examples can all undergo more iterations by simply varying these two factors. When calculating a guideline value, the WHO used the McCauley et al. study, 80% RSC, a 60 kg adult, and an intake of 2 L/day. These assumptions led the WHO to suggest a guideline value of 0.7 mg/L (rounded). Furthermore, this guideline is considered provisional due to the prevalence of chlorine dioxide disinfection and the possibility of treatment utilities regularly exceeding this value (WHO 2005).

Chlorate, similar to perchlorate, is a goitrogen and can decrease iodide uptake through competitive inhibition leading to the formation of goiters (enlargement of the thyroid). The USEPA cited the interference of perchlorate with iodine transport into the thyroid gland and low iodine uptake in general as the major health concern requiring a perchlorate MCL (USEPA 2011b), and thus might be

another factor EPA considers in regulating chlorate.

4. Technology Assessment

4.1 Analytical Methods

The ability to measure different chlorine compounds in water has improved tremendously over the past 50 years. In 1967, the measurement of chlorine dioxide, chlorite, and chlorate necessitated spectrometric determination of chlorine dioxide and total chlorite, iodimetric titration for total concentrations of chlorite and chlorate, and a Mohr titration for chloride (Hong and Rapson 1967). After spectrometric determination of the chlorine dioxide concentrations, the solution required bubbling with air to remove the chlorine dioxide before analysis of the other chlorine species was possible. In the mid-1980s, the lack of chlorate analysis in the latest edition of AWWA's *Standard Methods* prompted the development of new methods solely based on a series of titrations (Aieta et al. 1984; USEPA 1985). The best of the methods at this time achieved lower detection limits of 100 µg/L for chlorate, still far above the levels of chlorine dioxide (50 µg/L), chlorine (20 µg/L), and chlorite (20 µg/L) (Aieta et al. 1984).

The USEPA approves two ion chromatography methods for determining chlorate in drinking water: (1) USEPA Method 300.0 (USEPA 1999) and (2) USEPA Method 300.1 (USEPA 1998). There are also robust, accurate liquid chromatography tandem mass spectrometry methods available (Stanford et al. 2013), but they are not as yet approved for compliance monitoring. Chlorate samples are preserved with 50 mg/L EDA and can be stored up to 28 days. If collecting samples from treatment plants employing chlorine dioxide, the sample must be sparged with an inert gas at time of collection prior to EDA addition (USEPA Method 300.1 1999) in order to remove chlorine dioxide which could continue to form chlorite and chlorate. The UCMR3 set the minimum reporting level for chlorate at 20 µg/L (USEPA 2012).

4.2 Treatment Technologies

Generally, control of chlorate formation is preferable for reduction of chlorate concentrations as opposed to additional treatment for the removal of chlorate. There is not a standardized treatment process for removal of chlorate once formed. Based on this literature review, the published peer-reviewed papers chlorate treatment and removal are few and far between.

Approximately 35% of the chlorate in distribution systems where treatment plants use chlorine dioxide can be prevented by altering chlorine dioxide generation (Gallagher et al. 1994). The formation of chlorate ion in hypochlorite solutions is directly influenced by storage methods and handling techniques (Gordon et al. 1993; Gordon et al. 1995; Stanford et al. 2011). As reviewed earlier, the storage temperature and duration can greatly influence the residual concentrations of chlorate in finished water. With respect to dilution impacts, Gordon et al. (1995) addressed the importance in maintaining a pH 12-13 when diluting stock hypochlorite. Aside from onsite concerns addressed earlier, Stanford et al. (2011) cautioned that the quality of the stock hypochlorite delivered to a facility could impact chlorate concentrations due to the storage conditions after manufacture and prior to delivery.

There is no wide-spread residential self-treatment technology currently used to remove chlorate from home tap water once chlorate ions have formed. Granular activated carbon has shown promising

removal rates through physical, reversible sorption to the media (Gonce and Voudrias 1994). At the plant, research on chlorate removal by a membrane biofilm reactor achieved 99% removal of chlorate while having minimal effects on other water quality parameters, but several operational guidelines were necessary (Ziv-El and Rittmann 2009).

5. Health Levels of Potential Interest

A Safe Drinking Water Committee (NRC 1980) recommended a suggested no adverse effect level (SNARL) for chlorate of 210 µg/L and a no-observed-effect-level (NOEL) for hematological effects (based on cats) of 600 µg/kg/day. From the Lubbers et al. (1981) study, a LOEL of 36 µg/kg/day can be calculated.

In 2002, the California Office of Environmental Health Hazard Assessment (OEHHA) recommended a proposed action level of 200 µg/L chlorate based on a study by McCauley et al. (1995). An action level is not an enforceable standard. The recommended action level is intended to acknowledge potential co-exposures to other related drinking water disinfection byproducts which have similar toxic effects to that of chlorate. If the differences in water consumption data from rats is considered (males drink more), then the health protective levels for chlorate would be 210 µg/L and 290 µg/L for males and females, respectively. This value was rounded to 200 µg/L for the OEHHA recommended action level and is approximately 1/6th the concentrations used in the Lubbers et al. (1981) study. However, the current notification level for chlorate is 800 µg/L.

In 2002, Canada also published ambient water quality standards for chlorate (Warrington 2002) in which the recommended interim guideline for chlorate in drinking water was set as 2.4 mg/L to protect 5 kg infants. Finally, in 2005, the WHO published their background document for chlorate and chlorite, setting a provisional chlorate concentration at 0.7 mg/L, as explained earlier in the document. The definition of the RSC used to calculate the MCLG will have significant impact on the regulation and the percent of utilities exceeding the determined concentration.

6. Concluding Remarks

As of March, 2014, it is not completely clear how USEPA will handle chlorate in its preliminary third regulatory determination that is expected to be published later in 2014. However, chlorate should at least be considered a potential positive regulatory determination, i.e., a national regulation will eventually be developed.

The timing for such a national regulation is also not completely clear. The third regulatory determination would have to be finalized (maybe late 2015 or early 2016). Then, USEPA would have 24 months to publish a proposed regulation (late 2017 or early 2018), and 12 months thereafter to publish a final regulation (late 2018 or early 2019). Water systems would have the typical three years to come into compliance with the final regulation.

It is also not clear what the final Maximum Contaminant Level (MCL) might be. While the current chlorate HRL of 210 µg/L is certainly some form of current benchmark, establishing an MCL is complex process that takes into account several additional benefit-cost considerations. So even with the uncertainties about schedule and the final MCL, water systems may want to consider taking steps to

better understand their own chlorate levels in their drinking water.

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