Chlorate Challenges for Water Systems

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Chlorate, currently included in the US Environmental Protection Agency's monitoring of unregulated contaminants and on the contaminant candidate list, could potentially receive a regulatory determination in the near future. This article, using available literature along with past and current monitoring data, assesses the presence of chlorate in drinking water and the potential impact of its regulation. The article gives specific attention to the variety of threshold concentrations that appear most often in the literature—210, 700, and 840 µg/L—and evaluates the effect a regulatory requirement at each of these values would have on utilities. The research indicated that potential regulatory thresholds > 700 µg/L would be violated by only < 10% of utilities. The effects of regional conditions and type of disinfection used depend greatly on the adopted thresholds. Utilities in the southern region of the United States and those using chloramination are most at risk if a low maximum contaminant level is adopted.

Managing chlorate could become a challenge for water systems if the US Environmental Protection Agency (USEPA) establishes a maximum contaminant level (MCL) for this compound. Chlorate occurs in drinking water as a result of chlorine products used in treatment. Common sources of chlorate are the degradation of hypochlorite solutions, the on-site generation of hypochlorite, and the production and degradation of chlorine dioxide. Chlorate has been on the regulatory radar screen since the early 1990s, when it was part of the negotiated rulemaking for the proposed Stage 1 Disinfectants and Disinfection Byproducts (D/DBP) Rule (USEPA, 1994). Chlorate was not included in the final Stage 1 D/DBP Rule because the health effects data at that time were inadequate to establish a maximum contaminant level goal (MCLG) (USEPA, 1998). However, chlorate was discussed in those negotiations, and it is currently being discussed again for potential regulation.

Every five years, USEPA is required to publish a contaminant candidate list (CCL) itemizing chemicals of concern for evaluation and potential regulation. The third CCL, published in 2009, listed 104 chemicals of concern, including chlorate (USEPA, 2009). Chlorate is included in monitoring under the third round of the Unregulated Contaminant Monitoring Regulation (UCMR 3), which started in 2013 and will be completed at the end of 2015 (USEPA, 2012a). On a five-year cycle after each CCL is finalized, USEPA is required to make regulatory determinations on at least five contaminants.

Section 1412(b)(1)(A) of the Safe Drinking Water Act (SDWA) details three criteria that USEPA must consider in identifying new contaminants for potential regulation and in making regulatory determinations:

• The contaminant may have an adverse effect on the health of persons.

• The contaminant is known to occur or there is a substantial likelihood that the contaminant will occur in public water systems with a frequency and at levels of public health concern.

• In the sole judgment of the USEPA administrator, regulation of such contaminants presents a meaningful opportunity for health risk reduction for persons served by public water systems.

This article summarizes existing data related to the first two of these criteria—health effects and occurrence. The third criterion, whether a nationwide regulation provides a meaningful opportunity for risk reduction, is key for USEPA in making a regulatory determination. USEPA released the Preliminary Regulatory Determinations for Contaminants on the Third Drinking Water Contaminant Candidate List in October 2014, and a regulatory determination for chlorate was deferred to 2015 (USEPA, 2014a). This article also summarizes existing data on chlorate analytical methods, treatment, and control, all of which would be additional considerations for USEPA in developing a chlorate MCL.

A chlorate regulation would present a challenge for a growing number of water systems because the use of hypochlorite has increased as a result of safety, security, regulatory, or community concerns. Heightened security concerns since 9/11 and the regulatory requirements for risk management plans in Section 112(r) of the Clean Air Act are causing many utilities to move away from chlorine gas (AWWA, 2008a). In a 2007 survey of disinfection practices, 30% of utility respondents indicated that they had switched from chlorine gas to hypochlorite chlorination in the past eight to 10 years (AWWA, 2008a, 2008b). The majority of those who switched indicated they now use bulk liquid solutions (hypochlorite); only 6% of the 30% use on-site generation.

Keeping an appropriate amount of hypochlorite in storage to maintain disinfection during an emergency presents an additional

challenge. Too little hypochlorite in storage can compromise treatment, whereas aging stock continues to produce chlorate over time. A potential chlorate regulation would present a challenge from a regulatory development perspective in that these safety and security concerns would need to be balanced with the three SDWA criteria for identifying contaminants.

HEALTH EFFECTS

Chlorate is principally toxic through ingestion and inhalation, which typically lead to goitrogens and methemoglobin. A lethal oral dose is estimated to be as low as 20 g sodium chlorate, or 230 mg chlorate/kg of body weight (NAS, 1982). 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 eliminated by the kidneys, unchanged by processes within the body. High concentrations of chlorate impair the blood's ability to transport oxygen, and the toxic effects result from chlorate rupturing the membranes of red blood cells. The irreversible rupturing of red blood cells is followed by the formation of methemoglobin caused by the oxidation of free hemoglobin in the bloodstream. In most reported cases of chlorate poisoning, a drop in hemoglobin levels was observed, and methemoglobin was considered an early sign of intoxication (NAS, 1987).

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 gland). USEPA cited perchlorate's interference with iodine transport into the thyroid gland and low iodine uptake in general as the major health concerns in making a regulatory determination for perchlorate (USEPA, 2011a). This mode of action might be a factor in USEPA's consideration of a chlorate regulation.

To calculate a reference dose (RfD) from experimental studies that derive dose concentrations for no observed effect level (NOEL), no observed adverse effect level, (NOAEL), benchmark dose (BMD), or lowest observed adverse effect level (LOAEL), variations of Eq 1 are used. USEPA then uses the RfD to establish an MCLG by using Eq 2 (USEPA, 2003).

$$RfD = \frac{BMD \text{ or } LOAEL \text{ or } NOAEL}{UF \times MF} \tag{1}$$

in which RfD = reference dose, BMD = benchmark dose (in mg/kg/d), LOAEL = lowest observed adverse effect level (in mg/kg/d), NOAEL = no or low observed adverse effect level (in mg/kg/d), UF = uncertainty factor, and MF = modifying factor.

$$MCLG \left(\frac{mg}{L} \right) = \frac{Rfd \times BW \times RSC}{I} \tag{2}$$

in which BW = body weight (70 kg for adults, 10 kg for children, 4 kg for infants), RSC = the relative source contribution (fraction of the RfD received from drinking water), and I = daily intake of drinking water (2 L for adults, 1 L for children, 0.64 L for infants).

The most comprehensive study of the health effects of chlorate in drinking water was conducted by Lubbers et al (1981). Ten

male volunteers ingested single doses of 0.01, 0.1, 0.5, 1.0, 1.8, and 2.4 mg of chlorate ion in 1 L of drinking water per dose (for a total of 60 doses). Lubbers et al (1981) also had volunteers consume 36 µg/kg/d of chlorate over a 12-week period and observed them for an additional eight weeks. Despite this intensive study, no definitive detrimental physiological effect was determined. Therefore, the highest dose of chlorate, 36 µg/kg/d, was designated as the NOEL for the study.

According to the UCMR 3 Fact Sheet, the RfD for chlorate is set at 0.03 mg/kg/d and, on the basis of a 2004 study in rats, is associated with an enlarged thyroid gland and focal mineralization of thyroid gland follicles (USEPA, 2012b). This chronic toxicity study is cited in the National Toxicology Program's (NTP's) reregistration of inorganic chlorates (NTP, 2005; USEPA, 2006). The toxicity study cites several studies with NOAELs ranging from 0.9 to > 100 mg/kg/d, but no NOAEL was determined for non-neoplastic effects. Instead, a BMD of 0.9 mg/kg/d and a UF of 30 were used in calculating the chronic toxicity RfD of 0.03 mg/kg/d adopted by USEPA. A health reference level (HRL) is a benchmark against which USEPA evaluates occurrence data. MCLGs and HRLs are both calculated using Eq 2.

Using the RfD of 0.03 mg/kg/d, the HRL calculation is based on the assumptions of a 70-kg adult consuming 2 L/d of water and the default RSC of 20%, resulting in an HRL of 210 µg/L. Although USEPA's RSC default value of 20% was used in its calculation, the major exposure to chlorate comes from drinking water. An RSC of 80%, which some have argued is a more logical value, would increase the HRL to 840 µg/L (Cotruvo, 2014).

The World Health Organization (WHO) has a provisional guideline value that it calculated using a third study, a subchronic toxicity study conducted in rats by McCauley et al (1995). McCauley et al (1995) determined a NOAEL of 30 mg/kg/d on the basis of pituitary gland effects. Using a UF of 1,000, WHO also calculated an RfD of 0.03 mg/kg/d. This RfD, based on an RSC of 80% and a 60-kg adult ingesting 2 L/d of water led WHO to suggest a provisional guideline of 0.7 mg/L (WHO, 2005). The guideline was provisional because of concern that disinfection practices would likely cause the guideline value to be exceeded routinely (WHO, 2005). Similarly, Health Canada set a maximum acceptable limit of 1 mg/L chlorate, considering a lifetime exposure (Health Canada, 2005). The limits of both WHO and Health Canada are much greater than the USEPA HRL of 0.21 mg/L (210 µg/L). If USEPA adopts an 80% RSC in its calculations, the revised threshold of 840 µg/L would be in the same range as the thresholds of WHO and Health Canada.

Recently, USEPA released an update regarding the chlorate regulation (USEPA, 2014b). This document lists occurrence studies (e.g., Righi et al, 2012; Aggazzotti et al, 2004) that examine chlorate exposure in Italian populations. Righi et al (2012) concluded that chlorate exposure > 200 µg/L increased the risk of congenital anomalies, but Aggazzotti et al (2004) concluded that there was no increased risk for birth defects. Therefore, USEPA continues to rely on the 2005 NTP study as critical for establishing a chlorate RfD.

ANALYTICAL METHODS

The ability to measure different chlorine compounds in water has improved tremendously over the past 50 years. In the 1960s the measurement of chlorine dioxide, chlorite, and chlorate necessitated spectrometric determination of chlorine dioxide and chlorite concentrations, iodometric titration for concentrations of chlorite and chlorate, and a Mohr titration for chloride (Hong & Rapson, 1967). After spectrometric determination of chlorine dioxide concentration, 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 then-current edition of *Standard Methods for the Examination of Water and Wastewater* prompted the development of new methods based solely on a series of titrations (Aieta et al, 1984). As reported by Aieta et al (1984), the best of the methods at that time achieved lower detection limits of 100 µg/L for chlorate, still far above the detection levels for chlorine dioxide (50 µg/L), chlorine (20 µg/L), and chlorite (20 µg/L).

USEPA currently lists two ion chromatography methods for determining chlorate in drinking water: USEPA Method 300.0 (USEPA, 1993) and USEPA Method 300.1 (USEPA, 1997). Robust, accurate liquid chromatography–tandem mass spectrometry (LC–MS/MS) methods are also available (Stanford et al, 2013; Pisarenko et al, 2010; Li & George, 2005). An interlaboratory comparison indicated consistency among the USEPA-approved methods and the LC–MS/MS methods as reported by Stanford et al (2013). LC–MS/MS methods are more robust for complex matrixes such as hypochlorite solutions. Chlorate samples preserved with 50 mg/L ethylenediamine (EDA) can be stored up to 28 days. If samples are collected from treatment plants using chlorine dioxide, the samples require sparging with an inert gas at the time of collection prior to the addition of EDA (USEPA, 1997) to remove the chlorine dioxide, which otherwise could continue to form chlorite and chlorate. The UCMR 3 established a minimum reporting level (MRL) for chlorate of 20 µg/L (USEPA, 2012a) and specified the use of Method 300.1 for monitoring.

OCCURRENCE IN DRINKING WATER

Chlorate occurrence in drinking water has been evaluated several times in the past, but none of these assessments was as comprehensive as the current UCMR 3 monitoring initiative. Initial occurrence data for chlorate were summarized in the negotiated rulemaking for the proposed Stage 1 D/DBPR (USEPA, 1994). In a limited DBP field study conducted by USEPA during 1987–1991, chlorate concentrations ranging from 21 to 330 µg/L were found in all four (100%) samples from the treatment plants using chloride dioxide. In the plants not using chlorine dioxide, chlorate was found in 18 (60%) of the 30 samples from the plants, in concentrations ranging from < 10 to 660 µg/L. USEPA also found chlorate in three out of four (75%) of the samples from the distribution systems, in concentrations ranging from < 10 to 47 µg/L. Though the study was too limited for meaningful conclusions to be drawn, it highlighted the presence of chlorate in treated water.

The first comprehensive set of monitoring data for chlorate came from the Information Collection Rule (ICR), which was promulgated in 1996 (USEPA, 1996). ICR monitoring was conducted over 18 months from July 1997 to December 1998 to create a nationwide database (USEPA, 2011b). Under the ICR, 296 public water systems (PWSs) serving more than 100,000 people collected information pertaining to water quality, microbiological contamination, DBP occurrence and precursors, and treatment plant design and operating parameters (Wysock 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 database is unique in that it includes long-term monitoring for chlorate, whereas most monitoring programs cover a shorter period of time or a more limited number of samples. The MRL for chlorate under the ICR was 20 µg/L.

More recently, chlorate was included as part of the 2013–2015 UCMR 3 monitoring, projected to finish by December 2015 (USEPA, 2012a). Depending on the timing and USEPA's decision in its upcoming 2016 third Six-Year Review of Drinking Water Standards, the UCMR 3 data collection efforts should be completed before a potential chlorate regulation is proposed.

USEPA is updating and posting summaries of the UCMR 3 monitoring results on a regular basis (USEPA, 2014b); the latest set of UCMR 3 data was released in July 2014. USEPA is using the term "reference concentration" in its UCMR 3 reporting rather than HRL, but the reference concentration of 210 µg/L is the same as the previous HRL. The data available for this analysis, both ICR data and the July 2014 release of UCMR 3 data, are summarized in Table 1. Approximately 15% of the samples included in both data sets had chlorate concentrations above the HRL of 210 µg/L, and only 1% had concentrations greater than

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TABLE 1 Summary of ICR and UCMR 3 data

Monitoring Results	ICR Data* Number (%)	UCMR 3 Data† Number (%)
Samples	897	25,533
Systems	82	2,648‡
Samples > MRL§	747 (83)	14,356 (56)
Systems > MRL§	80 (98)	1,781 (67)
Samples > 210 µg/L	135 (15)	3,671 (14)
Systems > 210 µg/L	31 (38)	857 (32)
Samples > 700 µg/L	17 (21)	344 (1.3)
Systems > 700 µg/L	4 (5)	174 (7)
Samples > 840 µg/L	12 (1)	203 (0.8)
Systems > 840 µg/L	4 (5)	118 (4)

ICR—Information Collection Rule, MRL—maximum reporting level, UCMR 3—third round of Unregulated Contaminant Monitoring Regulation

*Finished water samples only
†Distribution system entry point and other monitoring samples as of July 2014
‡Represents 55–60% of the systems expected to report data under the UCMR 3
§20-µg/L MRL in both databases

Systems were evaluated using the utility's maximum reported concentration.

the higher 840-µg/L HRL calculated by Cotruvo (2014). For the following assessments, any nondetects in both the ICR and UCMR 3 databases were replaced by one-fourth of the MRL, similar to methods used by Alfredo et al (2014).

The maximum measured value associated with each PWS was used in the analysis of chlorate concentrations from both data sets to represent the highest potential for exposure. While 90th- or 95th-percentile values would have produced similar results, the purpose of this analysis was to determine the highest concentrations occurring at utilities. Figure 1 shows the distribution of available data for both the ICR and UCMR 3 databases as well as chlorate concentrations at the finished water's entry point into the distribution system, regardless of the disinfection method used. The limited number of PWSs in this analysis makes it difficult to assess any geographic trends in the ICR data (Figure 1, part A). In the UCMR 3 database, utilities reporting high concentrations of chlorate (greater than the WHO limit of 700 µg/L) are scattered throughout the country.

When these data were analyzed further, the maximum chlorate values associated with each utility in the UCMR 3 database were compared by grouping systems according to three sets of attributes: system size (Figure 2, part A), regional location (Figure 2, part B), and disinfection type (Figure 2, part C). The categories and abbreviations used by USEPA in association with these data were also adopted in the research reported in this article and are detailed in Table 2. The maximum chlorate concentration associated with each utility's distribution system entry point was used in analyzing regional location and system size. Only 1,822 (69%) of PWSs reported disinfection data for the distribution system entry point; therefore, only this subset was considered in the following disinfection analyses. Despite the fact that only 69% of the utilities reported data, many utilities varied disinfection throughout the treatment plant, and this resulted in reports of varying chlorate concentrations depending on the type of disinfection used in the treatment facility and at the distribution system entry point. A total of 2,260 disinfection-related chlorate concentrations were reported, and this full data set was used in the disinfection analysis shown in Figure 2, part C. The 95th percentile of each group plotted in Figure 2 was < 1,000 µg/L.

The UCMR 3 monitoring requirements apply to water systems serving more than 10,000 people, limiting the study primarily to these larger systems, as reflected in the number of data points for each size category shown in Table 2. Because the categories for very small and small systems contained few data points, trends were considered only for the categories containing medium to very large systems. As shown in Figure 2, part A, the larger the system, the greater the probability that chlorate was present. The map of chlorate concentrations throughout the United States (Figure 1, part B) was not very conclusive; the boxplot for US region (Figure 2, part B) helps to indicate any trends that might be present. To further test the regional association, the chi-square test was used to test whether chlorate concentrations depended on the water system's regional location. The calculated chi-square value was well within the critical range ($\chi^2_{obtained} > > \chi^2_{critical} = 16.919$, 9 degrees of freedom, $\alpha = 0.05$), suggesting a correlation but

not causation. Of the PWSs with maximum chlorate concentrations of > 700 µg/L, 43% were located in the South.

Figure 2, part C, groups utilities according to type of disinfection used. Most of the utilities that were using no disinfection had chlorate concentrations < 210 µg/L. There is more than a chance association between chlorate concentration and disinfection type ($\chi^2_{obtained} > > \chi^2_{critical} = 36$, 24 degrees of freedom, $\alpha = 0.05$). Chloramination practices correlated not only the highest chlorate concentrations but also the largest variability in chlorate concentrations; 60% of facilities that produced chloramines on site had chlorate concentrations > 210 µg/L. These results indicate that it is extremely important for utilities to monitor the disinfection process and control unwanted by-products. More than 51% (38 utilities) of the systems with chlorate concentrations > 840 µg/L used hypochlorite generated off site for chlorination. Only five utilities practicing on-site generation of hypochlorite measured chlorate concentrations > 840 µg/L. The two groups with the highest chlorate concentrations consisted of utilities that produced chloramines and chlorine dioxide on site, and both groups were most predominant in the South. The Midwest, the region with the lowest chlorate concentrations, was dominated by utilities using gaseous chlorination and included very few treatment facilities that generated chloramines or chlorine dioxide on site.

Chlorine gas, the disinfectant many utilities are abandoning because of security considerations, produces the lowest concentrations of chlorate in treated water. In the 2007 disinfectant-specific survey, chlorine gas remained the most prevalent disinfectant in use; however, 25% of the utilities surveyed planned to switch to hypochlorite (either bulk or generated on site) in the future (AWWA, 2008a, 2008b). The utilities that continued to use chlorine gas cited its reliability and cost as the main drivers for not switching (AWWA, 2008b).

Although the ICR database is limited in its ability to allow the same analyses as those just described because of the number of utilities throughout the country reporting chlorate concentrations, it allows temporal comparisons within water systems because chlorine dioxide systems were sampled every month and hypochlorite systems were sampled quarterly during the entire 18-month monitoring period. One utility using each type of disinfection was selected at random from the Northeast and South for comparison. Figure 3 consists of four plots of chlorate concentrations over time—one plot for each PWS. The New Jersey system was sampled in duplicate for quality control, and the average value was used in this analysis. If a 210-µg/L threshold had been enforced during this time, all but the Georgia utility would have accumulated violations. The seasonality and the variation of chlorate concentrations can affect how a regulation is enforced.

Before the UCMR 3 monitoring program, comprehensive sets of chlorate data were sparse except for the ICR data, and they were limited to systems using chlorine dioxide or hypochlorite as a disinfectant. The current relevance of the ICR data for the ongoing regulatory development process is questionable because the monitoring was conducted in 1997–1998 and thus does not account for the increased use of hypochlorite since then. USEPA's most recent regulatory update reports that the agency is relying

FIGURE 1   Distribution of maximum chlorate concentrations in finished water reported in (A) the ICR database and (B) the UCMR 3 database as of the April 2014 data release
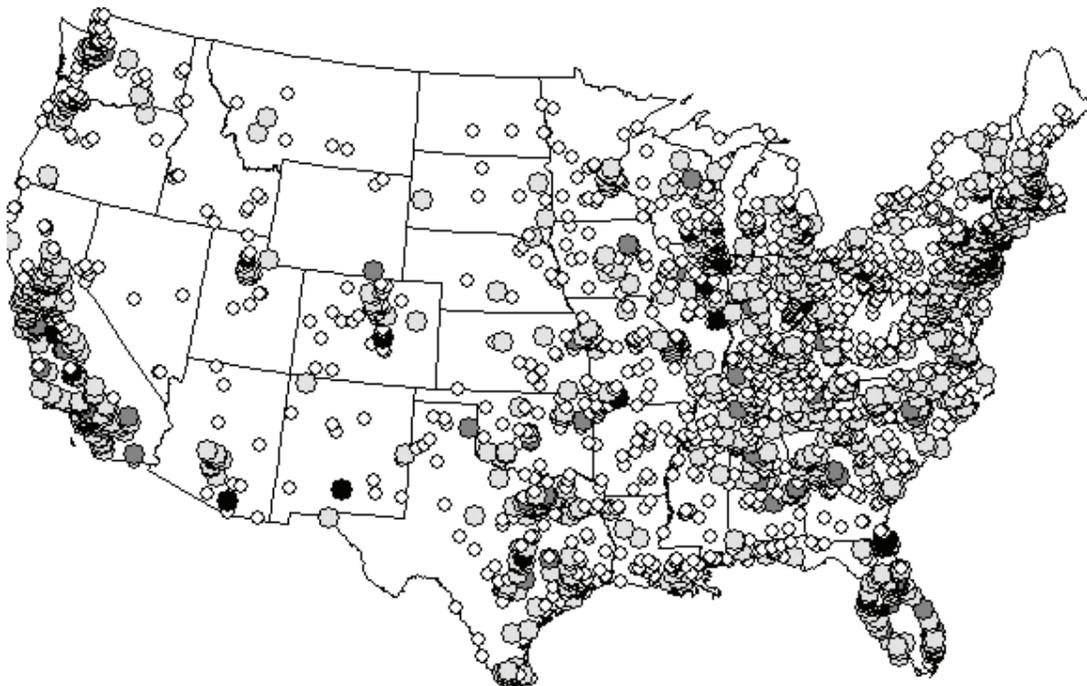
Chlorate Concentration—$\mu g/L$
○ < 210
○ 211–700
◐ 701–1,000
● > 1,000

A ICR Database

B UCMR 3 Database

ICR—Information Collection Rule, UCMR 3—third round of Unregulated Contaminant Monitoring Regulation

on this database for analysis (USEPA, 2014b). What an analysis of the ICR data highlights is that chlorate can vary significantly over time, and thus regulatory considerations such as compliance with running annual averages versus individual samples are also important.

TREATMENT AND CONTROL

Generally, minimizing chlorate concentrations by controlling the formation of chlorate is preferable to adding treatment for chlorate removal. There is no standardized treatment process for removing chlorate once it has formed. There is some indication that granular activated carbon (GAC) can partially remove chlorate through physical, reversible sorption to the media. Gonce and Voudrias (1994) achieved adsorption capacities of 4.9 mg chlorate per gram of GAC for an influent chlorate concentration of 5 mg/L. However, desorption occurred as efficiently as adsorption in their research, indicating the need for careful monitoring of finished water quality. Some research has

indicated that chlorate removal can be achieved under anaerobic conditions by a membrane biofilm reactor (Ziv-El & Rittmann, 2009a), a process potentially limited to use at contaminated groundwater sites rather than in conventional surface water treatment. In hydrogen-limited systems in the Ziv-El and Rittmann (2009a) investigations, chlorate was lower in the sequential order of oxidation and removal after oxygen, nitrate, and nitrite. Anion exchange resins can also be potential means for removing chlorate, though competition from other anions in water (sulfate, carbonate, nitrate, perchlorate, chloride), natural organic matter, and seasonal water quality will all affect the efficacy and useful life of the resin. Reverse osmosis is also effective for chlorate removal but is very energy-intensive and creates a waste brine stream requiring disposal. Much of the research in the literature focused on chlorite and perchlorate removal, with chlorate monitoring mentioned only as a side note (Blute et al, 2013; Ziv-El & Rittmann, 2009b; Health Canada, 2005; Katz & Narkis, 2001; Steinbergs, 1986).

FIGURE 2 UCMR 3 maximum chlorate concentrations at each utility, analyzed by (A) system size, (B) region, and (C) disinfection type
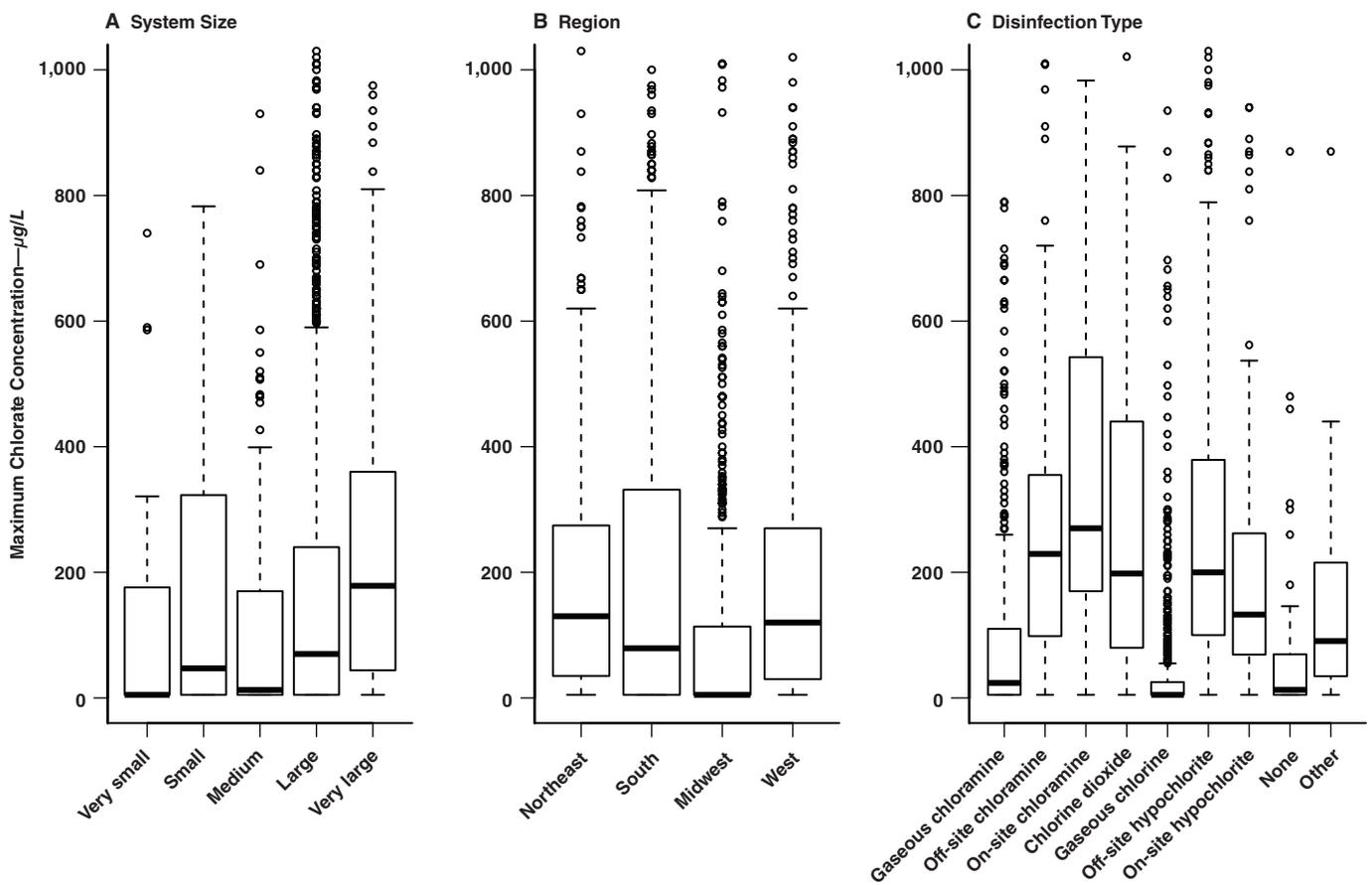
UCMR 3—third round of Unregulated Contaminant Monitoring Regulation

Box plots represent the 25th, 50th, and 75th percentiles. Outliers are included as individual data points on each plot.

Data from the July 2014 UCMR 3 data release

TABLE 2	Details of the categories used to cluster utilities in the UCMR 3 database

Number of Systems	System Size and Population Served
32	Very small: 25–500
97	Small: 501–3,000
155	Medium: 3,301–10,000
2,007	Large: 10,001–100,000
280	Very large: > 100,000
Region	
423	Northeast: Conn., D.C., Del., Mass., Maine, N.H., N.J., N.Y., Pa., R.I., Vt.
952	South: Ala., Ark., Fla., Ga., Ky., La., Md., Miss., N.C., Okla., S.C., Tenn., Texas, Va., W.V.
621	Midwest: Iowa, Ill., Ind., Kans., Mich., Minn., Mo., N.D., Neb., Ohio, S.D., Wis.
569	West: Alaska, Ariz., Calif., Colo., Hawaii, Idaho, Mont., N.Mex., Nev., Ore., Utah, Wash., Wyo.
Type of Disinfection Used	
342	Chloramine (formed from gaseous chlorine)
213	Chloramine (generated off site)
114	Chloramine (generated on site)
88	Chlorine dioxide
705	Gaseous chlorine
617	Hypochlorite (generated off site)
168	Hypochlorite (generated on site)
109	None (no disinfection used)
26	Other (disinfectants other than those reported, excluding ozone)

UCMR 3—third round of Unregulated Contaminant Monitoring Regulation

Utilities using chlorine dioxide can reduce approximately 35% of the chlorate in their distribution systems by altering chlorine dioxide generation (Gallagher et al, 1994), though substantial amounts of chlorate will still be formed during degradation of the chlorine dioxide. The formation of chlorate ion in hypochlorite solutions is directly influenced by storage methods and handling techniques at utilities using bulk hypochlorite (Stanford et al, 2011; Gordon et al, 1995, 1993). Dilution of bulk hypochlorite with softened water and pH control in the 12–13 range, or careful temperature control, can help minimize the amount of chlorate formed during storage. Additionally, Stanford et al (2011) cautioned that the quality of stock hypochlorite delivered to a facility could affect chlorate concentrations as a result of storage conditions after manufacture and prior to delivery.

At systems that generate hypochlorite on site, production of chlorate during the generation process is highly variable even from the same generator, and there is no apparent difference in chlorate production among brands or types of solutions produced (Stanford et al, 2013). Hypochlorite generated on site may be a significant source of chlorate at some utilities, as seen in the UCMR 3 data. Work published by Stanford et al (2013) indicated that 33% of the tested systems that generated hypochlorite on site had > 210 µg/L of chlorate in their finished water with a 5-mg/L chlorine dosage; with a chlorine dosage of

10 mg/L, 66% of the systems tested would have exceeded the 210-µg/L concentration. However, only two of the 29 systems tested exceeded the WHO guideline of 700 µg/L, indicating that USEPA's final regulatory determination could have a potentially significant impact on water utilities, depending on the MCL selected. Though further study is needed and generator-specific operating procedures need to be established, the concept of brine conditioning and temperature control may become a viable means for controlling chlorate formation in the future (unpublished data from the National Science Foundation's Small Business Innovation Research). However, brine conditioning must also be carefully balanced with the negative effect that reducing pH will have on chlorine stability in the treated water.

The strategies described in this article constitute several potential methods for minimizing chlorate formation, which appears to be the best means of keeping chlorate out of finished water (as opposed to treatment). Utilities can access an online tool available from AWWA to better understand the effects of various storage and handling practices for bulk hypochlorite solutions (AWWA, 2012). Future research should focus on methods for minimizing chlorate production in hypochlorite solutions that are generated on site.

REGULATORY CHALLENGES RELATED TO CHLORATE

In its Preliminary Regulatory Determinations for Contaminants on the Third Drinking Water Contaminant Candidate List (USEPA, 2014a), USEPA included chlorate (and nitrosamines) in a collective review of the Microbial and Disinfection Byproduct (M/DBP) Regulations, as part of the third Six-Year Review of Existing Regulations, expected to be proposed in 2015. Therefore, any potential chlorate regulation would be complicated by the multi-dimensional question of whether the M/DBP Regulations should be revised or how they might be revised. As a result, USEPA could face its own regulatory challenges, depending on the threshold value used in the development of a potential chlorate MCL. An MCL of 210 µg/L would significantly increase the nationwide cost of compliance compared with an MCL in the range of WHO's guideline of 700 µg/L or an 80% RSC of 840 µg/L.

Past regulatory determinations provide some insight as to how USEPA might address chlorate in upcoming regulatory determinations. In its first two regulatory determinations, USEPA decided that if the contaminant was detected in concentrations above the HRL in fewer than 50 water systems, it did not warrant a federal regulation because this would not provide a meaningful opportunity for risk reduction as mandated by the SDWA (Roberson, 2012). The UCMR 3 data released in July 2014 indicate that more than 50 systems nationwide have chlorate concentrations above the HRL, whether occurrence is based on the WHO guideline of 700 µg/L (174 systems) or an 80% RSC of 840 µg/L (118 systems). However, the UCMR 3 data that are currently publicly available include monitoring results only from systems serving > 10,000 people, so nationwide occurrence for all PWSs will be higher.

Nevertheless, detections above the HRL in fewer than 50 systems do not constitute a bright line for determining whether a federal regulation is warranted. The SDWA gives the USEPA administrator some discretion in decision-making during the regulatory development process. The upper limit of that line is

FIGURE 3   Seasonal variations in ICR chlorate measurements at PWS treatment plants practicing chlorine dioxide disinfection (A and B) and hypochlorination (C and D)

A New Jersey–Chlorine Dioxide

B Georgia–Chlorine Dioxide

C Delaware–Hypochlorite

D Alabama–Hypochlorite
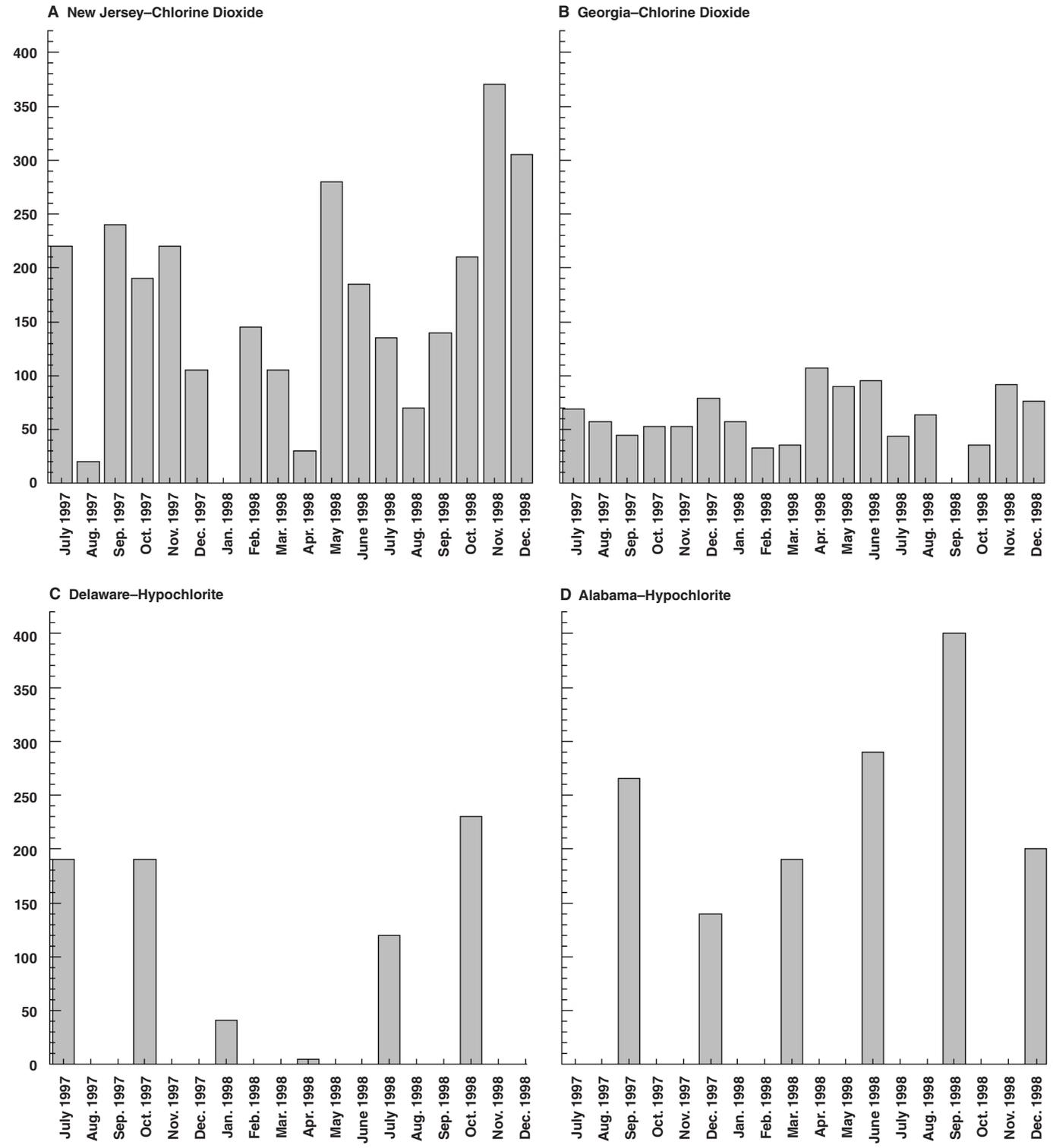
ICR—Information Collection Rule, PWS—public water system

likely higher than 50 systems and might be more in the range of 1,000–2,000 systems to warrant a federal regulation. Between the floor of 50 systems and the ceiling of 1,000–2,000 systems is a gray area in which the USEPA administrator must take into account several factors, including the population and number of systems affected, the geographic distribution of occurrence, and the potential RSC of the contaminant.

The timing for a federal chlorate regulation is still unknown. The third regulatory determination will conclude in late 2015 or early 2016, and the M/DBP regulatory review in which USEPA has now placed chlorate is scheduled for a similar end date. 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 most likely be given the typical three-year period to comply with the final regulation.

Another uncertainty is the concentration threshold of a final MCL. Though the current chlorate HRL of 210 µg/L is certainly some form of a benchmark, establishing an MCL is a complex process that takes into account several additional benefit–cost considerations. Balancing the risks previously discussed will likely be one of the additional considerations. Under the SDWA, the USEPA administrator has the flexibility to set an MCL at a value higher than is strictly feasible and has done so in the past for arsenic and uranium.

In addition to WHO, 13 countries and territories have established standards > 210 µg/L (WHO, 2013). The standards set by Canada (1,000 µg/L) and New Zealand (800 µg/L) are higher than WHO's provisional guideline of 700 µg/L, and those of Japan (600 µg/L) and the Dominican Republic (200 µg/L) are lower. The other nine use WHO's provisional guideline. So the worldwide trend generally points toward a higher regulatory or guideline value than USEPA's HRL of 210 µg/L.

A recent letter to the editor published in *Journal AWWA* provides additional insight into USEPA's 210-µg/L HRL (Cotruvo, 2014). HRLs are neither a potential USEPA standard nor a health advisory but rather an ICR screening benchmark that originated from a chlorate pesticide registration. So although the chlorate HRL of 210 µg/L is based on an RSC of 20%, an 80% RSC could be more appropriate because the dominant source of chlorate exposure is drinking water. Adopting an 80% RSC would increase the HRL to 840 µg/L. Though these two HRLs (210 and 840 µg/L) might be considered the boundary conditions for a potential chlorate regulation, any prediction about where a chlorate MCL might end up would be premature at this time.

Another consideration for a potential chlorate regulation would be the compliance determination. Most DBPs are regulated on the basis of a chronic health effects endpoint, with compliance based on a running annual average. However, because USEPA could potentially consider a drop in hemoglobin levels to be an acute health effect, a compliance determination could be based on an individual sample. This decision would present additional compliance challenges for water systems using hypochlorite.

Even with uncertainties about the schedule, the compliance determination, and the final MCL, utility officials should consider taking steps to better understand their water system's chlorate concentrations and temporal variability. Chlorate presents some unique compliance challenges for water systems because no routine treatment technology exists for removing it. Though almost all regulated drinking water contaminants can be removed by one or more existing treatment technologies, the key to compliance with a potential chlorate regulation is to prevent the compound's formation. Although some mitigation techniques are being explored for systems that generate hypochlorite on site, most of the control strategies revolve around proper storage and handling of bulk hypochlorite and carefully controlled production of chlorine dioxide.

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REFERENCES

Aggazzotti, G.; Righi, E.; Fantuzzi, G.; Biasotti, B.; Ravera, G.; Kanitz, S.; Barbone, F.; Sansebastiano, G.; Battaglia, M.A.; Leoni, V.; Fabiani, L.; Triassi, M.; & Sciacca, S., 2004. Chlorination By-products (CBPs) in Drinking Water and Adverse Pregnancy Outcomes in Italy. *Journal of Water and Health,* 2:4:233.

Aieta, E.M.; Roberts, P.V.; & Hernandez, M., 1984. Determination of Chlorine Dioxide, Chlorine, Chlorite, and Chlorate in Water. *Journal AWWA,* 76:1:64.

Alfredo, K.A.; Seidel, C.; & Roberson, J.A., 2014. Reviewing the Occurrence Data Used in the Revised Arsenic Rule. *Journal AWWA,* 106:3:E139. http://dx.doi.org/10.5942/jawwa.2014.106.0038.

AWWA, 2012. Hypochlorite Assessment Model. www.awwa.org/ResourcesTools/WaterandWastewaterUtilityManagement/HypochloriteAssessmentModel.aspx (accessed April 2013).

AWWA Disinfection Systems Committee, 2008a. Committee Report: Disinfection Survey, Part 1—Recent Changes, Current Practices, and Water Quality. *Journal AWWA,* 100:10:76.

AWWA Disinfection Systems Committee, 2008b. Committee Report: Disinfection Survey, Part 2—Alternatives, Experiences, and Future Plans. *Journal AWWA,* 100:11:110.

Blute, N.; Pedersen, D.W.; Wu, X.; & Means, E., 2013. Demonstration Testing of Nitrification Control Using Chlorite in Irvine, Calif. *Journal AWWA,* 105:4:E207. http://dx.doi.org/10.5942/jawwa.2013.105.0051.

Cotruvo, J.A., 2014. Health-Based Drinking Water Calculations Are Not Absolute. Letters to the Editor. *Journal AWWA,* 106:4:18. http://dx.doi.org/10.5942/jawwa.2014.106.0068.

Gallagher, D.L.; Hoehn, R.C.; & Dietrich, A.M., 1994. Sources, Occurrence, and Control of Chlorine Dioxide By-product Residuals in Drinking Water. AWWA Research Foundation, Denver.

Gonce, N. & Voudrias, E.A., 1994. Removal of Chlorite and Chlorate Ions From Water Using Granular Activated Carbon. *Water Research,* 28:5:1059. http://dx.doi.org/10.1016/0043-1354(94)90191-0.

Gordon, G; Bubnis, B.; & Adam, L.C., 1995. Minimizing Chlorate Ion Formation. *Journal AWWA,* 87:6:97.

Gordon, G.; Adam, L.C.; Bubnis, B.P.; Hoyt, B.; Gillette, S.J.; & Wilczak, A., 1993. Controlling the Formation of Chlorate Ion in Liquid Hypochlorite Feedstocks. *Journal AWWA,* 85:9: 89.

Health Canada, 2005. *Chlorite and Chlorate in Drinking Water.* Federal-Provincial-Territorial Committee on Drinking Water, Health Canada, Ottawa.

Hong, C.C.; & Rapson, W.H., 1967. Analyses of Chlorine Dioxide, Chlorous Acid, Chlorite, Chlorate, and Chloride in Composite Mixtures. *Canadian Journal of Chemistry,* 46:2061. http://dx.doi.org/10.1139/v68-336.

Katz, A. & Narkis, N., 2001. Removal of Chlorine Dioxide Disinfection By-products by Ferrous Salts. *Water Research,* 35:1:101. http://dx.doi.org/10.1016/S0043-1354(00)00250-5.

Li, Y. & George, E.J., 2005. Analysis of Perchlorate in Water by Reversed-Phase LC/ESI-MS/MS Using an Internal Standard Technique. *Analytical Chemistry,* 77:14:4453. http://dx.doi.org/10.1021/ac0500986.

Lubbers, J.R.; Chauhan, S.; & Bianchine, J.R., 1981. Controlled Clinical Evaluations of Chlorine Dioxide, Chlorite and Chlorate in Man. *Fundamental and Applied Toxicology,* 1:4:334. http://dx.doi.org/10.1016/S0272-0590(81)80042-5.

McCauley, P.T.; Robinson, M.; Daniel, F.B; & Olson, G.R., 1995. The Effects of Subchronic Chlorate Exposure in Sprague-Dawley Rats. *Drug and Chemical Toxicology,* 18:2-3:185. http://dx.doi.org/10.3109/01480549509014320.

NAS (National Academy of Sciences), 1987. *Drinking Water and Health: Disinfectants and Disinfectant By-Products,* Vol. 7. National Academies Press, Washington.

NAS, 1982. *Drinking Water and Health,* Vol. 4. National Academies Press, Washington.

NTP (National Toxicology Program), 2005. *Toxicology and Carcinogenesis Studies of Sodium Chlorate* (CAS NO. 7775-09-9) in *F344/N Rats and B6C3F1 Mice (Drinking Water Studies*). NTP Technical Report 06-4457. National Institutes of Health, Bethesda, Md.

Pisarenko, A.N.; Stanford, B.D.; Quiñones, O.; Pacey, G.E.; & Snyder, S.A., 2010. Rapid Analysis of Perchlorate, Chlorate and Bromate Ions in Concentrated Sodium Hypochlorite Solutions. *Analytica Chimica Acta,* 659:1–2:216. http://dx.doi.org/10.1016/j.aca.2009.11.061.

Righi, E.; Bechtold, P.; Tortorici, D.; Lauriola, P.; Calzolari, E.; Astolfi, G.; Nieuwenhuijsen, M.J.; Fantuzzi, G.; & Aggazzotti, G., 2012.Trihalomethanes, Chlorite, Chlorate in Drinking Water and Risk of Congenital Anomalies: A Population-Based Case Control Study in Northern Italy. *Environmental Research,* 116:66. http://dx.doi.org/10.1016/j.envres.2012.04.014.

Roberson, J.A., 2012. Informing Regulatory Decisions Using National Occurrence Data. *Journal AWWA,* 104:3:E194. http://dx.doi.org/10.5942/jawwa.2012.104.0036.

Stanford, B.D.; Pisarenko, A.N.; Dryer, D.J.; Ziegler-Holady, J.C.; Gamage, S.; Quinones, O.; Vanderford, B.J.; & Dickenson, E.R.V., 2013. Chlorate, Perchlorate, and Bromate in Onsite-Generated Hypochlorite Systems. *Journal AWWA,* 105:3:E93. http://dx.doi.org/10.5942/jawwa.2013.105.0014.

Stanford, B.D.; Pisarenko, A.N.; Snyder, S.A.; & Gordon, G., 2011. Perchlorate, Bromate, and Chlorate in Hypochlorite Solutions: Guidelines for Utilities. *Journal AWWA,* 103:6:71.

Steinbergs, C.Z., 1986. Removal of By-products of Chlorine and Chlorine Dioxide at a Hemodialysis Center. *Journal AWWA,* 78:6:94.

USEPA (US Environmental Protection Agency), 2014a. Announcement of Preliminary Regulatory Determinations for Contaminants on the Third Drinking Water Contaminant Candidate List. *Federal Register,* 79:202:62715.

USEPA, 2014b. The Third Unregulated Contaminant Monitoring Rule (UCMR 3): Data Summary. http://water.epa.gov/lawsregs/rulesregs/sdwa/ucmr/upload/epa815s14001.pdf. Last Updated January 2014 (accessed Apr. 22, 2014). Link for ongoing releases: http://water.epa.gov/lawsregs/rulesregs/sdwa/ucmr/data.cfm#ucmr2013.

USEPA, 2012a. Unregulated Contaminant Monitoring Regulation 3 (UCMR 3) for Public Water Systems. *Federal Register,* 77:85:26071.

USEPA, 2012b. The Third Unregulated Contaminant Monitoring Rule (UCMR 3): Fact Sheet for Assessment Monitoring of List 1 Contaminants. EPA 815-F-12-003. USEPA Office of Water, Washington.

USEPA, 2011a. Drinking Water: Regulatory Determination on Perchlorate. *Federal Register,* 76:29:7762.

USEPA, 2011b. ICR Envirofacts. www.epa.gov/enviro/html/icr/ (accessed July 2014). Last updated 2011.

USEPA, 2009. Drinking Water Contaminant Candidate List 3. *Federal Register,* 74:194:51850.

USEPA, 2006. Reregistration Eligibility Decision (RED) for Inorganic Chlorates. EPA 738-R-06-014. USEPA Office of Water, Washington.

USEPA, 2003. *Six-Year Review—Chemical Contaminants: Health Effects Technical Support Document.* EPA 822-R0-3008. USEPA Office of Water, Washington.

USEPA, 1998. Stage 1 Disinfectants and Disinfection Byproducts Rule. Final Rule. *Federal Register,* 63:241:69390.

USEPA, 1997. Method 300.1: Determination of Inorganic Anions in Drinking Water by Ion Chromatography. National Exposure Research Laboratory, Cincinnati, Ohio.

USEPA, 1996. Information Collection Rule. *Federal Register,* 61:94:24354.

USEPA, 1994. Stage 1 Disinfectants and Disinfection Byproducts Rule. Proposed Rule. *Federal Register,* 59:145:38668.

USEPA, 1993. Method 300.0. Determination of Inorganic Anions in Drinking Water by Ion Chromatography. Revision 2.1. EPA/600/R-98/118. USEPA Office of Research and Development, Cincinnati.

WHO (World Health Organization), 2013. *Report on Regulations and Standards for Drinking Water Quality.* Draft Report. World Health Organization, Geneva.

WHO, 2005. *Chlorite and Chlorate in Drinking-Water: Background Document for the Development of WHO Guidelines for Drinking-Water Quality.* World Health Organization, Geneva.

Wysock, B.M.; Cummins, M.D.; Fair, P.S.; Feige, M.A.; Sorrell, R.K.; Walasek, J.B.; Allgeier, S.C.; Shukairy, H.M.; Karapondo, M.S.; & Bohl, B.J., 2002. ICR Implementation and Data Collection Challenges. *Information Collection Rule Data Analysis* (M.J. McGuire, J.L. McLain, & A. Obolensky, editors). USEPA & AWWA Research Foundation, Denver.

Ziv-El, M.C. & Rittmann, B.E., 2009a. Systematic Evaluation of Nitrate and Perchlorate Bioreduction Kinetics in Groundwater Using a Hydrogen-Based Membrane Biofilm Reactor. *Water Research,* 43:1:173. http://dx.doi.org/10.1016/j.watres.2008.09.035.

Ziv-El, M.C. & Rittmann, B.E., 2009b. Water Quality Assessment of Groundwater Treated With a Membrane Biofilm Reactor. *Journal AWWA,* 101:12:77.