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Occurrence of perchlorate in sodium hypochlorite

RESPONDING TO THE DETECTION OF PERCHLORATE IN SODIUM HYPOCHLORITE BY THE MASSACHUSETTS DEPARTMENT OF ENVIRONMENTAL PROTECTION, NSF INTERNATIONAL SURVEYED FOR THE CONTAMINANT IN DRINKING WATER TREATMENT CHEMICALS FROM PRODUCTION FACILITIES ACROSS THE UNITED STATES AND CANADA.

Perchlorate is both a synthetic and a naturally occurring chemical. Most of the perchlorate that is manufactured in the United States is used as the primary ingredient of solid rocket propellant. Wastes from the manufacture and improper disposal of perchlorate-containing chemicals are increasingly being discovered in soil and water (USEPA, 2007).

An additional source of perchlorate in drinking water has been found to occur through the use of sodium hypochlorite. The Massachusetts Department of Environmental Protection (MDEP) has reported that significant levels of perchlorate can be detected in sodium hypochlorite samples that have aged for a few weeks (MDEP, 2005). Sodium hypochlorite as delivered to one utility had a perchlorate concentration of 0.2 µg/L in the product, but the level of perchlorate rose to 6,750 µg/L after the product had aged for 26 days.

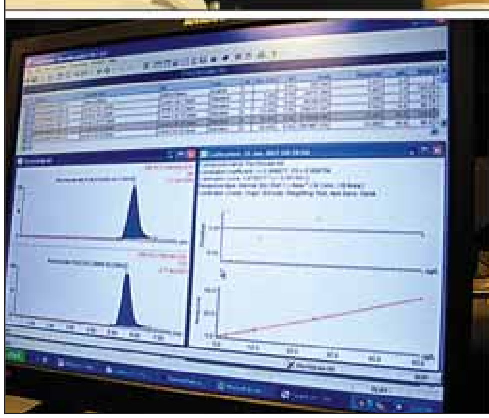
INVESTIGATION OF WATER TREATMENT CHEMICALS BEGAN IN 2005

In 2005 NSF International began analyzing samples of drinking water treatment chemicals for the contaminant perchlorate. These samples were collected as part of the annual testing requirement to support NSF certification of the treatment chemical to NSF/American National Standards Institute Standard 60: Drinking Water Treatment Chemicals—Health Effects (NSF/ANSI, 2005). Samples collected included not only sodium hypochlorite but other types of chemicals as well. NSF 60 currently requires testing of sodium hypochlorite samples for regulated metals, volatile organic compounds, and bromate.

NSF continued the investigation of sodium hypochlorite through July 2006, resulting in the analysis of more than 67% of NSF-certified manufacturers across North America. The levels of perchlorate reported here reflect potential at-the-tap concentrations calculated in accordance with the proce-

Aliquots of the sodium hypochlorite samples collected at manufacturers' facilities were placed in 40-mL amber glass vials and stored in the dark prior to testing.

Perchlorate concentrations were determined by a liquid chromatography/mass spectrometry technique based on US Environmental Protection Agency method 331.0.



dures in NSF 60. These "normalization" calculations project potential at-the-tap concentrations by assuming the treatment chemical is dosed at the maximum use level (MUL) for which it was certified. Typically the MUL for sodium hypochlorite products is equivalent to dosing 10 mg/L of total chlorine into water. Although this concentration is significantly above the US Environmental Protection Agency (USEPA) maximum residual disinfectant level goal of 4.0 mg/L, it provides a worst-case evaluation of the sodium hypochlorite by accounting for other potential uses such as prechlorination during water treatment and use during shock chlorination of water systems.

Perchlorate health effects. Perchlorate affects the ability of the thyroid gland to take up iodine (ATSDR, 2005). Iodine is needed to make thyroid hormones that are released into the blood and regulate many body functions. Perchlorate is considered harmful to health when its inhibition of iodine uptake is great enough to affect the thyroid. There is concern that human exposure to higher amounts of perchlorate for a long time may lower the level of thyroid activity and lead to hypothyroidism. Low levels of thyroid hormones in the blood may adversely affect the skin, cardiovascular system, pulmonary system, kidneys, gastrointestinal tract, liver, blood, neuromuscular system, nervous system, skeleton, male and female reproductive systems, and numerous endocrine organs. Studies in animals have shown that the thyroid gland is the main target of perchlorate toxicity. Animal studies provided inconclusive results regarding effects of perchlorate on the immune system. Perchlorate did not affect reproduction in rats, according to one study.

Perchlorate regulation and guidance criteria. In October 2008 the USEPA announced a preliminary determination on the regulation of perchlorate. After conducting an extensive review of scientific data related to the health effects of exposure to perchlorate from drinking water and other sources, USEPA "... found that in over 99% of public drinking water systems, perchlorate was not at levels of public health concern. Therefore, based on the Safe Drinking Water Act criteria, the agency determined there is not a 'meaningful opportunity for health risk reduction' through a national drinking water regulation" (USEPA, 2008). USEPA will make a final determination for perchlorate after a 30-day public comment period. The agency also intends to issue a health advisory at the time it issues the final regulatory determination in order to assist states with their local response for perchlorate.

At the state level, perchlorate guidance criteria of 14 µg/L in Arizona, 5 µg/L in New York, and 1 µg/L in Maryland and New Mexico have been adopted, along with action levels of 18 µg/L in New York and Nevada and 4 µg/L in Texas (Bull et al, 2004). California has established a perchlorate maximum contaminant level (MCL) of 0.006 mg/L (CDPH, 2007), and Massachusetts has established a perchlorate MCL of 0.002 mg/L (MDEP, 2006). For the purposes of estimating the effect of perchlorate contamination, the current research used the lowest of these values, in other words, 1 µg/L.

Perchlorate is considered harmful to health when its inhibition of iodine uptake is great enough to affect the thyroid.

SAMPLES NORMALLY COLLECTED DURING UNANNOUNCED AUDITS TESTED FOR PERCHLORATE

As part of NSF's certification program for drinking water treatment chemicals, unannounced audits of manufacturing sites are performed annually, and samples of certified treatment chemicals are taken from recent production or retains. NSF used portions of these normally collected samples for this research on perchlorate. Once the samples were received at NSF, aliquots were placed in 40-mL amber glass vials and stored in the dark at room temperature before testing.

Laboratory analysis. The analysis for perchlorate was performed according to a modified USEPA method 331.0, Determination of Perchlorate in Drinking Water by Liquid Chromatography Electrospray Ionization Mass Spectrometry (USEPA, 2005). Method 331.0 is a method for analyzing drinking water. All method requirements relevant to the analysis of sodium hypochlorite rather than drinking water were included; the modification of this method at NSF related to modification of the quality control requirements.

Method 331.0 allows for identification by either tandem mass spectrometry mode or single ion monitoring mode using dual ions (masses 99 and 101). In this research, quantification was performed by internal standard calibration using the mass 101 ion. Results were reported in µg/L for liquid samples. In sodium hypochlorite, the average detection level for perchlorate was 250 µg/L.

Approximately one third of the samples tested were additionally tested on multiple days to determine the rate of change in perchlorate concentration as the sodium hypochlorite aged. Samples were maintained in the dark and at room temperature between analysis days.

164 CHEMICAL SAMPLES TESTED

Through July 2006, perchlorate testing was performed on 164 samples of drinking water treatment chemicals collected from 102 manufacturing locations. Of the 37 types of chemicals tested, perchlorate was detected in only two: sodium hydroxide and sodium hypochlorite (Table 1).

Of the 27 sodium hydroxide samples, 22 (81%) had perchlorate levels reported as nondetectable; in the remaining five samples, perchlorate concentrations ranged from 0.01 to 0.12 µg/L (Table 2).

The occurrence of perchlorate in sodium hypochlorite was a more common finding. Perchlorate was detected in more than 91% of the samples tested, at levels ranging from 0.03 to 29 µg/L. Table 3 groups the results by concentration range, including a running average of samples containing perchlorate at levels less than or equal to the level of perchlorate in the range.

Of greater significance was the correlation between the age of the sodium hypochlorite and the level of perchlorate detected. Figure 1 shows the results of testing on samples with a known date of manufacture. Results, plotted by sample age at the time of analysis, clearly demonstrated a trend of increasing perchlorate concentration as the hypochlorite product aged.

Three of the samples tested yielded perchlorate concentrations of 8.8, 11, and 29 µg/L, significantly greater than the levels found in other samples; the 29-µg/L value does not appear in Figure 1 because the date of manufacture had not been established. Because these concentrations were significantly outside the observed levels of perchlorate formation in the other sodium hypochlorite samples tested, the authors believe that contamination of one of the component materials used to manufacture the sodium hypochlorite may be the primary perchlorate source.

Table 4 summarizes the occurrences of perchlorate by sodium hypochlorite age range. All of the samples tested within the first 30 days of production had a normalized perchlorate concentration below 1 µg/L. Of those samples tested between 30 and 45 days after production, 97% had perchlorate concentrations below 1 µg/L and just 3% had levels exceeding that value. Between 45 and 60 days after production, however, 8% of samples tested showed perchlorate concentrations exceeding 1 µg/L, and by 90 days after production, perchlorate levels in 84% of samples exceeded 1 µg/L.

Twenty-three of the samples tested were analyzed for perchlorate content on multiple days to provide insight into the rate of increase. Samples were maintained in the dark and at room temperature between analyses. Results of the "over time" analysis are shown in Figure 2. The plots demonstrated a consistent rate of increase across multiple sample sources.

Portions of three of the sodium hypochlorite samples that were tested over time were diluted at a ratio of 1:2 with deionized water and also tested over time to determine whether the rate of perchlorate formation was significantly different in diluted form. As shown in Figure 3, a comparison of the full-strength and diluted samples found that the full-strength sodium

TABLE 1 Summary of samples tested by chemical type

Chemical	Samples—*n*	Samples With Perchlorate Detected—*n*	Samples With Perchlorate Detected %
Aluminum chloride	1		
Aluminum sulfate	2		
Ammonium hydroxide	3		
Bentonite	1		
Calcium hydroxide	1		
Calcium hypochlorite	2		
Calcium oxide	2		
Carbon dioxide	1		
Copper sulfate	2		
Ferric chloride	2		
Ferric sulfate	2		
Ferrous chloride	1		
Ferrous sulfate	1		
Fluorosilicic acid	1		
Fluosilicic acid	1		
Hydrochloric acid	1		
Hydrofluosilicic acid	1		
Hydrogen peroxide	1		
Phosphoric acid	3		
Polyaluminum silicate sulfate	1		
Potassium carbonate	1		
Sodium bicarbonate	1		
Sodium bisulfite	2		
Sodium carbonate	1		
Sodium chloride	2		
Sodium chlorite	1		
Sodium fluoride	1		
Sodium hexametaphosphate	1		
Sodium hydroxide	27	5	19
Sodium hypochlorite	82	75	91
Sodium polyphosphates, glassy	3		
Sodium silicate	5		
Sodium trimetaphosphate	1		
Sulfuric acid	2		
Trichloroisocyanuric acid	1		
Zinc chloride	1		
Zinc orthophosphate	2		
Total	164		

TABLE 2 Perchlorate occurrences in sodium hydroxide samples

Samples—*n*	Perchlorate in Chemical—*μg/kg*	Perchlorate At the Tap—*μg/L*
22	ND (250)	ND (0.03–0.05)
1	700	0.07
1	900	0.09
1	600	0.12
1	160	0.03
1	110	0.01

n—number, ND—not detected

ND results were below the detection level of the analytical procedure as identified in the parentheses. For calculation of the values in column 3, the level of perchlorate found in the chemical was multiplied by the maximum use level (MUL) certified for the individual chemical. Not all sodium hydroxides have the same certified MUL.

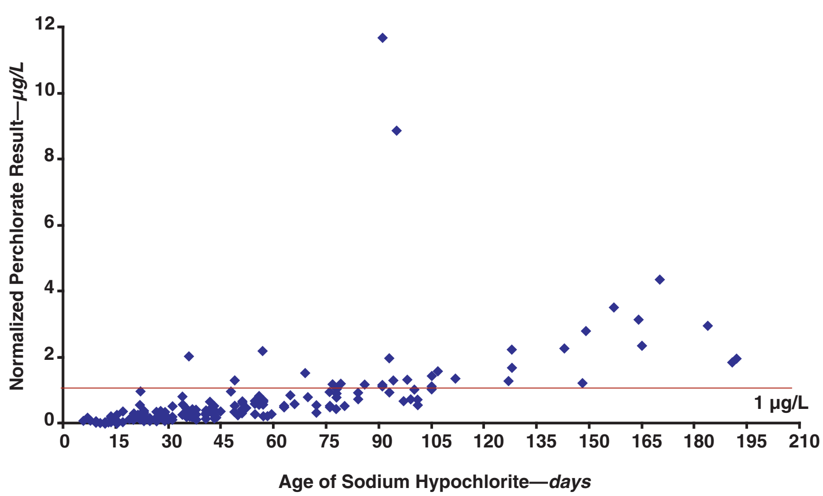
TABLE 3 Perchlorate concentration range in sodium hypochlorite samples*

Concentration Range—*μg/L*	Samples—*n*	Samples—*%*	Samples—Running %
ND	7	9	9
> ND–1.0	42	51	60
> 1–2	9	11	71
> 2–3	15	18	89
> 3–4	4	5	94
> 4–5	2	2	96
> 5–6	0	0	96
> 6–7	0	0	96
> 7–8	0	0	96
> 8	3	4	100
Total	82	100	

n—number, ND—nondetected

*At-the-tap in μg/L

FIGURE 1 Perchlorate in sodium hypochlorite (normalized to at-the-tap values)



hypochlorite generated perchlorate at a rate six to nine times faster than the same product diluted to half strength.

Three of the sodium hypochlorite samples were also evaluated over time to determine whether the level of bromate, chlorate, or chlorite also changed with age. No significant trend was noted for increasing or decreasing bromate levels. This was expected because almost all of the bromine in chlorine and the bromide in sodium hydroxide—the primary ingredients in sodium hypochlorite—are quickly converted to bromate at the pH of sodium hypochlorite (Chlorine Institute, 2004). The levels of chlorate and chlorite generally increased with age, but separate research is needed to better quantify that behavior.

Several factors were identified as contributing to variability in these results.

- Composite samples were collected from manufacturers across one or more days of the manufacturer's production retains. For the purposes of this study, the "date of manufacture" corresponding to these samples was the date of the earliest retain of the composite sample. This practice particularly affected the precise correlation between age of the sodium hypochlorite and the corresponding perchlorate level.
- The way the samples were stored and shipped to NSF prior to storage and analysis at NSF also added to the variability, given that both temperature and light have been reported to affect the rate of perchlorate formation.
- Results were normalized to the maximum use level (MUL) for the chemical in the NSF listing. The MULs were not necessarily proportional to the strength of the sodium hypochlorite nor were they directly associated with the level of chlorate. The levels of perchlorate in this study have been presented as potential at-the-tap levels because this was the

primary concern being addressed through NSF 60 evaluations.

SUMMARY AND CONCLUSION

Testing affirmed the recurrent presence of perchlorate in sodium hypochlorite. This appeared to be associated with the natural formation of perchlorate from chlorate, but results suggested there may also be occurrences of perchlorate attributable to contamination from component ingredients or manufacturing processes.

The data compiled by NSF to date supported the data previously collected by MDEP on perchlorate occurrence in sodium hypochlorite. The data also supported the MDEP's conclusion that the perchlorate levels were probably not a concern for most water utilities that use sodium hypochlorite within a few weeks of production. However, perchlorate occurrence may be a concern for water systems that store sodium hypochlorite for longer periods or have residual levels of aged chemical in storage tanks that may contaminate new shipments.

The data further indicated that NSF 60 should address perchlorate contamination. Perchlorate should be a required parameter for all sodium hypochlorite products, and a single product allowable concentration for perchlorate needs to be established in the standard. In addition, the data suggested a need for expiration dates on all sodium hypochlorite shipments to water utilities as well as on small containers of bleach that may be used by small systems.

For utilities that routinely use sodium hypochlorite supplies within 45 days of manufacture, the contribution of perchlorate is likely to be negligible unless there is some contamination of the original ingre-

TABLE 4 Perchlorate summary by age of NaOCl

Age of NaOCl at Testing *days after manufacture*	Analysis—*n*	Perchlorate > 1 µg/L—*n*	Perchlorate < 1 µg/L %	Perchlorate > 1 µg/L %
≤ 30	53	0	100	0
> 30 to ≤ 45	32	1	97	3
> 45 to ≤ 60	25	2	92	8
> 60 to ≤ 90	24	4	83	17
> 90	32	27	16	84
Total	166			

n—number, NaOCl—sodium hypochlorite

FIGURE 2 Perchlorate levels in sodium hypochlorite (normalized to at-the-tap values)

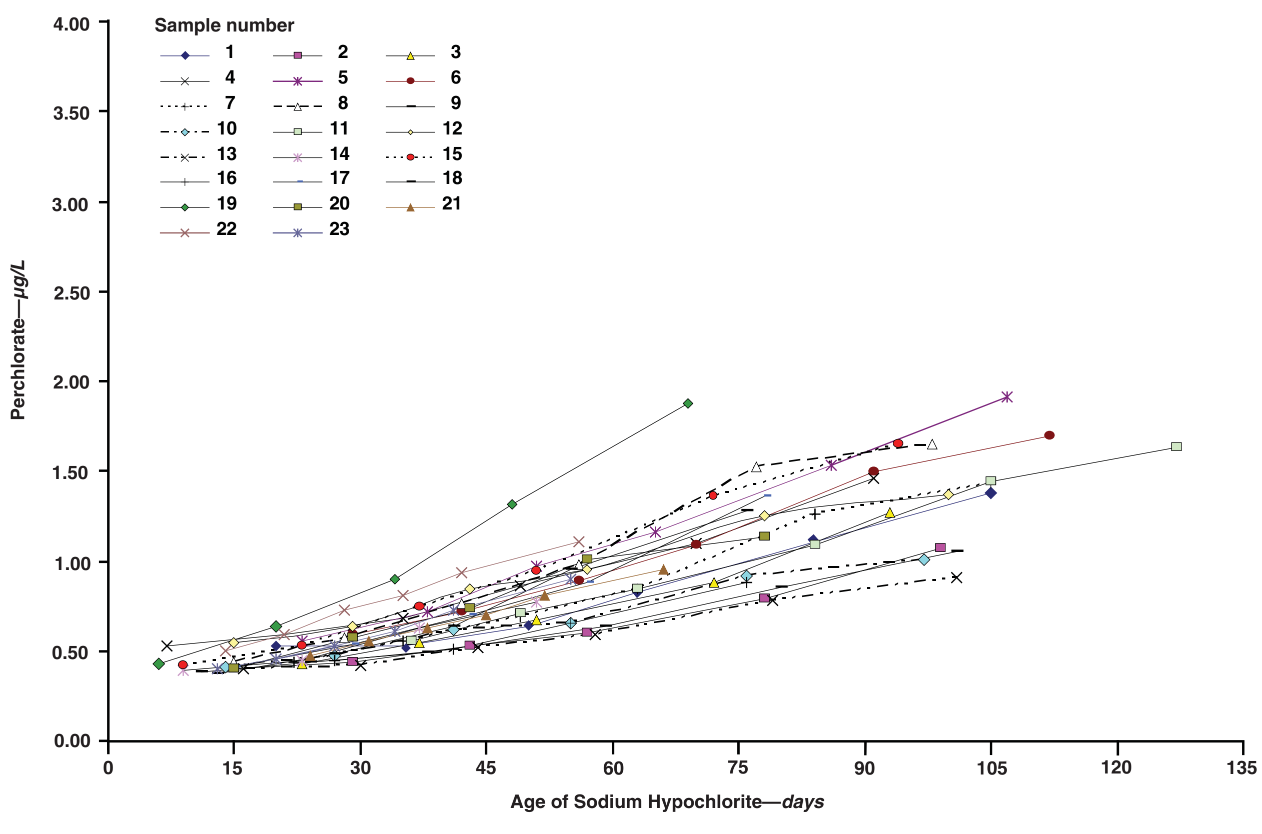
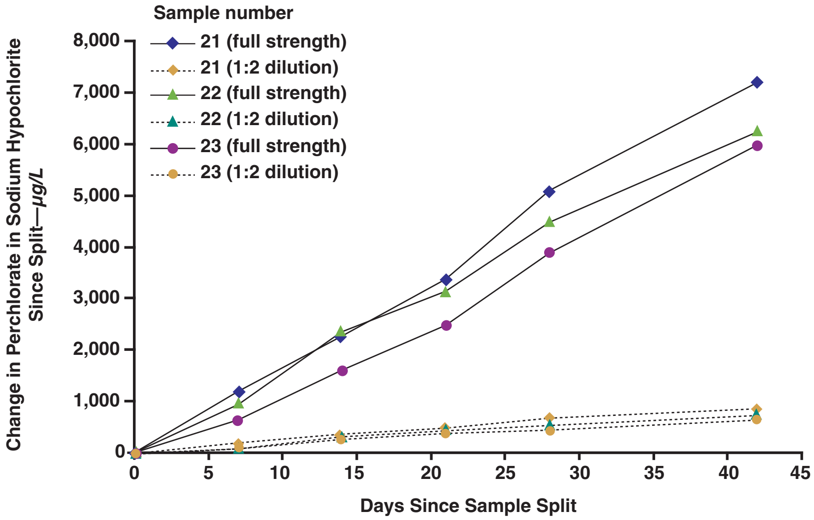


FIGURE 3 Comparison of perchlorate formation rates for full-strength and diluted (1:2 ratio) sodium hypochlorite



dients. Utilities or small systems that store sodium hypochlorite for longer periods may encounter significant levels of perchlorate in the finished drinking water. To minimize the perchlorate risk, sodium hypochlorite should be stored in the dark at cool temperatures, diluted if possible, and used within a few weeks of manufacture. Storage tanks and piping should also be emptied of aged material and flushed to minimize the potential for contamination.

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REFERENCES

ATSDR (Agency for Toxic Substances and Disease Registry), 2005. Perchlorates. Div. of Toxicology & Envir. Med. ToxFAQs™, September. http://www.atsdr.cdc.gov/tfacts162.pdf.

Bull, R.J.; Chang, A.C.; Cranor, C.F.; Shank, R.C.; & Trussell, R., 2004. Perchlorate in Drinking Water: A Science and Policy Review. Urban Water Research Center, University of California, Irvine.

CDPH (California Department of Public Health), 2007. Perchlorate in Drinking Water. http://www.cdph.ca.gov/certlic/drinkingwater/Pages/Perchlorate.aspx., accessed Nov. 17, 2007.

Chlorine Institute, 2004. Bromate in Sodium Hypochlorite Potable Water Treatment. Chlorine Institute, Arlington, Va., http://www.chlorineinstitute.org/files/FileDownloads/BromateinNaOCl-PotableWaterTreatment.pdf.

MDEP (Massachusetts Department of Environmental Protection), 2006. 7/28/06 Revisions to 310 CMR 22.00. Inorganic Chemical Maximum Contaminant Levels, Monitoring Requirements, and Analytical Methods. http://www.mass.gov/dep/water/laws/perchlorate-310CMR22-07282006.doc.

MDEP (Massachusetts Department of Environmental Protection), 2005. The Occurrence and Sources of Perchlorate in Massachusetts. Draft Report, http://www.mass.gov/dep/cleanup/sites/percsour.pdf.

NSF/ANSI (NSF International/American National Standards Institute), 2005. NSF/ANSI Standard 60. Drinking Water Treatment Chemicals—Health Effects. NSF Intl., Ann Arbor, Mich.

USEPA (US Environmental Protection Agency), 2008. Regulatory Determinations for Priority Contaminants on the Second Drinking Water Contaminant Candidate List. October 2008 Preliminary Regulatory Determination for Perchlorate. http://www.epa.gov/safewater/ccl/reg_determine2.html-perchlorate.

USEPA, 2007. Drinking Water Contaminants. Perchlorate. http://www.epa.gov/safewater/contaminants/unregulated/perchlorate.html.

USEPA, 2005. Method 331.0—Determination of Perchlorate in Drinking Water by Liquid Chromatography Electrospray Ionization Mass Spectrometry. EPA 815-R-05-007, Cincinnati. http://www.epa.gov/safewater/methods/pdfs/methods/met331_0.pdf.