Immediate Action Levels for Water Treatment Plant Chemicals

Formerly Referred to as
"Memorandum on Treatment Chemicals as Do Not Drink or Use Guidance"

(2011 update)

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Immediate Action Levels for Water Treatment Plant Chemicals

MassDEP has derived **Immediate Action Levels** for a number of indicator parameters for commonly used treatment chemicals. These limits are intended for use by plant operators to identify when a situation involving chemical over-feeds or use of the wrong chemical has occurred of sufficient gravity to require the implementation of emergency response procedures. **The concentrations associated with the Immediate Action Levels are associated with the potential for immediate, serious adverse health effects. Response measures should include immediate notifications not to drink or use the water, taking the water with the problem offline if possible and correcting the problem.**

These parameters are frequently and routinely monitored in the treatment plant. In addition to the levels listed in the table on the following page, water delivered to the entry point of the distribution system is also required to meet various other federal and state standards and guidelines (see listing at: http://www.mass.gov/dep/water/laws/regulati.htm#chems).

This 2010 version of the guidance differs from the 2008 version by including the guidance for treatment plants disinfecting with chlorine dioxide.

IMMEDIATE ACTION LEVELS FOR WATER TREATMENT PLANT CHEMICALS AND MONITORING PARAMETERS

Treatment Chemical	Indicator Chemical/Parameter	Immediate Action Level, mg/L	Applicable to:
acids, caustics	pH – HIGH pH - LOW	**> 11** **< 4.5**	all
sodium fluoride, fluorosilicic acid, sodium fluorosilicate	fluoride	**10 mg/L**	all
chlorine, chloramines	free residual chlorine	**25 mg/L**	all
chlorine dioxide	chlorine dioxide	**2 mg/L** **72 mg/L**	women of childbearing age, infants and young children other healthy members of the population
	chlorite	**2 mg/L** **72 mg/L**	women of childbearing age, infants and young children other healthy members of the population
	pH free residual chlorine	**<4.5 (low pH)** **>11.0 (high pH)** **25 mg/L (free chlorine)**	all
	pH ORP* (sample location on chlorine dioxide delivery line)	**employ facility- specific limits.**	all

* ORP = oxidation-reduction potential .

The following information describes the bases for the values presented in the table.

I. Recommended pH Guidelines

> **A pH value of 11 is recommended as an upper do not use/do not drink value. Solutions with pH values at or above this value, lacking other information on the factors noted below, should be considered to present a significant risk of skin and eye irritation and possible exacerbation of skin disorders. In order to avoid potential ocular irritant effects and reversible damage, water with a pH of below 4.5 should not be used.**

pH is a measure of the effective concentration of hydrogen ions and is expressed on a scale that ranges from 0-14 units. Because it uses a log scale, a change of one pH unit corresponds to a change in the hydrogen ion concentration of a factor of 10. USEPA recommends that drinking waters be maintained at pH values between 6.5 and 8.5 to avoid adverse aesthetic impacts. Adjustments to somewhat higher pH's (e.g. up to 9) are sometimes used to minimize leaching of metals, in particular lead, into drinking water from pipes within the distribution system.

Strong acids typically cause tissue damage by denaturing proteins. Strong bases can both denature proteins and saponify fats, which facilitates tissue penetration and damage. Effects may range from mild irritation to severe burns. The likelihood and severity of effect depends on the pH; the buffering capacity of the water; the amount or volume of exposure; the duration and frequency of exposure; and individual sensitivity.

High pH

Water with significantly elevated pH values can irritate, and at high enough values, severely damage mucus membranes, the eye, throat and skin if consumed or used for washing. Elevated pH can also cause the water to feel slippery and taste alkali (bitter), make it difficult to get soaps and detergents to lather, and lead to the formation of precipitate deposits in pipes and on clothing and dishes. Elevated pH water could also impact the effectiveness of certain medicines.

According the World Health Organization eye irritation and exacerbation of skin disorders have been associated with exposures to water with pH values greater than 11 (WHO, 1996). Solutions with pH values of 12.5 or greater have been reported to cause significant tissue damage including esophageal ulceration when consumed. Such effects can be serious and of longer duration and would warrant immediate medical evaluation.

Low pH

Under the Safe Drinking Water Act the lower limit secondary maximum contaminant level for pH was established at 6.5. This value was selected to minimize the corrosivity of drinking water in the distribution system and thus minimize leaching of lead, cadmium, copper, iron, and zinc from metal pipes and the mobilization of asbestos from corrosion of cement asbestos pipes.

Although many foods, including lemon juice and carbonated beverages may have pH values as low as 2.5, Potts (1991) reports that "as the pH of buffered solutions applied to the human eye is decreased from 7.4, the onset of discomfort begins at about pH 4.5. Between pH 4.5 and 3.5, one creates punctate breaks in the corneal epithelium that are stainable with fluorescein but heal in a few hours' time."

Thus, to avoid the potential for ocular irritant effects and reversible damage it is recommended that water with a pH below 4.5 not be used.

II. Recommended Fluoride Guideline

A fluoride value of 10 mg/L is recommended as a do not drink or use limit.

Concentrations below 10 mg/L are protective of potential nausea, vomiting and gastric pain that may occur at higher values. A fluoride value of <10 mg/L is recommended to also protect against skin rashes and itching that may occur as a result of dermal contact with the water.

The acute health effects of fluoride may include severe nausea, vomiting, excess saliva production, abdominal pain and diarrhea. More serious acute health effects are convulsions, irregular heartbeat and coma. After being ingested into the stomach, 50% of sodium fluoride is typically converted into hydrofluoric acid (HF), which is absorbed through the mucous membrane of the stomach at a rate 1,000,000 times greater than F^-. Fluoride then circulates in the body and returns to the mouth through the salivary glands. HF formation in the stomach is pH dependent, with more being formed at lower pH values. The U.S. Center for Disease Control (CDC 1995) has recommended that, if the fluoride level in a community water system exceeds 10 mg/L, the fluoridation system be turned off immediately in order to protect public health. At 10 mg F/L, it is estimated that a 2 year old, weighing 10 kilograms and drinking one liter of water would receive a fluoride dose that is associated with gastrointestinal symptoms, requiring treatment. At higher levels more severe health effects would occur.

Infants (ages birth to 12 months) who are fed reconstituted infant formula mixed with tap water as a primary source of nutrition represent a high risk group, mainly due to their higher ingestion rate per smaller unit of body weights. The American Dental Association recommends the use of fluoride-free water for mixing formula. Infants and young children are also more susceptible to the effects of fluoride on the thyroid gland (endocrine disruption) and to dental fluorosis (NRC, 2006).

There is little information about the effects of fluoride from non-drinking water exposures. One community health study reported that skin contact with 50 mg/L fluoride caused itching and skin rashes (Petersen et al., 1988). No other studies on the water concentration of fluoride and dermal effects were found.

10 mg F/L of water is recommended as a do not use value for the following reasons:

- 50 mg/L fluoride is a frank effect level and dermal effects at lower concentrations, including 10 mg/L, cannot be ruled out;
- If water at concentrations higher than 10 mg F/L is available to the public, people may drink the water and become ill.

The US Environmental Protection Agency (US EPA 1986) has set an enforceable drinking water standard for fluoride of 4 mg/L (some people who drink water containing fluoride in excess of this level over many years could get bone disease, including pain and tenderness of the bones). The EPA has also set a secondary fluoride standard of 2 mg/L to protect against dental fluorosis. Dental fluorosis, in its moderate or severe forms, may result in a brown staining and/or pitting of the permanent teeth. This problem occurs only in developing teeth, before they erupt from the gums. Children under nine should not drink water that has more than 2 mg/L of fluoride on a long-term basis. The EPA MCL of 4.0 mg/L is based on chronic effects and risk balancing. The Secondary MCL of 2.0 mg/L has been set to protect against dental fluorosis.

III. Recommended Limits for Free Chorine for the Disinfectants Chlorine and Chloramines

> **A free chlorine concentration of 25 mg/L should be used as an Immediate Action Level for water treatment facilities employing chlorine or chloramines as disinfectants.**

Facilities which treat with the oxidants chlorine or monochloramine monitor in real- or near real-time the amount of total and or free residual chlorine in the water that they treat. An acute exposure limit for chlorine only will be identified to be used with facilities that employ these disinfectants.

The US EPA’s Drinking Water Criteria Document for Chlorine (US EPA 1994) summarizes the health effects of exposure to chlorine which is a strong respiratory and dermal irritant.

There is a federal standard of 4 mg/L for chlorine in drinking water known as a Maximum Residual Disinfectant Level (MRDL). An MRDL is "a level of a disinfectant added for water treatment that may not be exceeded at the consumer's tap without an unacceptable possibility of adverse health effects. For chlorine and chloramines, a PWS is in compliance with the MRDL when the running annual average of monthly averages of samples taken in the distribution system, computed quarterly, is less than or equal to the MRDL. MRDLs are enforceable in the same manner as maximum contaminant levels under Section 1412 of the Safe Drinking Water Act. Notwithstanding the MRDLs, operators may increase residual disinfectant levels of chlorine or chloramines (but not chlorine dioxide) in the distribution system to a level and for a time necessary to protect public health to address specific microbiological contamination problems caused by circumstances such as distribution line breaks, storm runoff events, source water contamination, or cross-connections." (US EPA 2000a). <u>Since compliance is based on an annual average, the MRDL does not apply to individual samples that are allowed to be higher than the MRDL</u> (US EPA 1994). Because of the manner of derivation of the MRDLs and the fact that they can be exceeded in drinking water treatment systems, they do not appear as appropriate values to use as a cutoff value requiring issuance of "Do Not Drink" or "Do Not Bathe" notices during upset conditions.

The MRDL was set using toxicological data from a chronic rat study. The value was derived to be protective of human health with chronic exposure and includes uncertainty factors. It therefore is not the sort of number that could serve as an emergency level from a toxicological point of view. During an upset emergency, exposures would be of short-term or acute duration. From an operational perspective it seems best to have a limit representing conditions where adverse effects would be expected if exposures took place.

The US EPA identifies Health Advisory values for short-term exposures to chemicals. They did not find suitable information for determining a One-day Health Advisory (HA) for chlorine. They did find suitable data to allow them to derive a 10-day HA value of 3 mg/L (US EPA 2006). EPA notes that in the absence of a unique 1-day value, the 10-day value is a conservative estimate for a 1-day exposure. The values do not appear to be appropriate for use as an acute shutdown or "Do Not Drink" level because they are based on an animal no adverse effects level (NOAEL) which was numerically reduced by the application of a total of 100-fold of uncertainty factors applied for interspecies extrapolation and recognition of the variation in sensitivity across the population. Temporary exceedance of the 1-day value would not necessarily reflect a critical enough situation to warrant shutting down a water system or issuing use limitation notices. However, the information on which the HA is based can serve as a basis for identifying an acute exposure limit not to be exceeded. The current 10-day HA value is based upon a NOAEL (25 mg/kg/d or 200 mg/L) from a mouse study by (Blabaum and Nichols 1956). There was an absence of gross lesions, histological abnormalities and changes in weight or growth over the 50-day exposure period. Ideally, an acute limit for use at a treatment plant should be near an effect level for a chemical. In order to translate the NOAEL used for the 10-day HA value into an effect level, it can be multiplied by a factor of 10 to reflect the standard conversion factor used when extrapolating lowest adverse effect levels (LOAELs) to NOAELS (in those cases dividing by the factor of 10 to reduce the

LOAEL dose to a NOAEL dose). The LOAEL values can then be numerically decreased by dividing by 10 and 10 for interspecies extrapolation and sensitivity in the population. The resulting drinking water concentration for a child (assumed 10 kg body weight ingesting 1L of water per day) would be **<u>25 mg/L</u>**. In Figure 1 this value is graphically contrasted against other reported effects levels from the literature to put it in perspective.

This concentration should also be used to indicate the likely potential for dermal and ocular irritation through uses of the drinking water in the home for bathing or showering, although no dose-response information for these types of acute exposures has been located. Operational guidance for the treatment of swimming pools and whirlpool baths may provide some perspective. Recommended free chlorine concentrations in properly maintained swimming pools disinfected with chlorine (in several different forms) range from 1.5 – 2.0 mg/L. The Centers for Disease Control's recommended levels in spas and

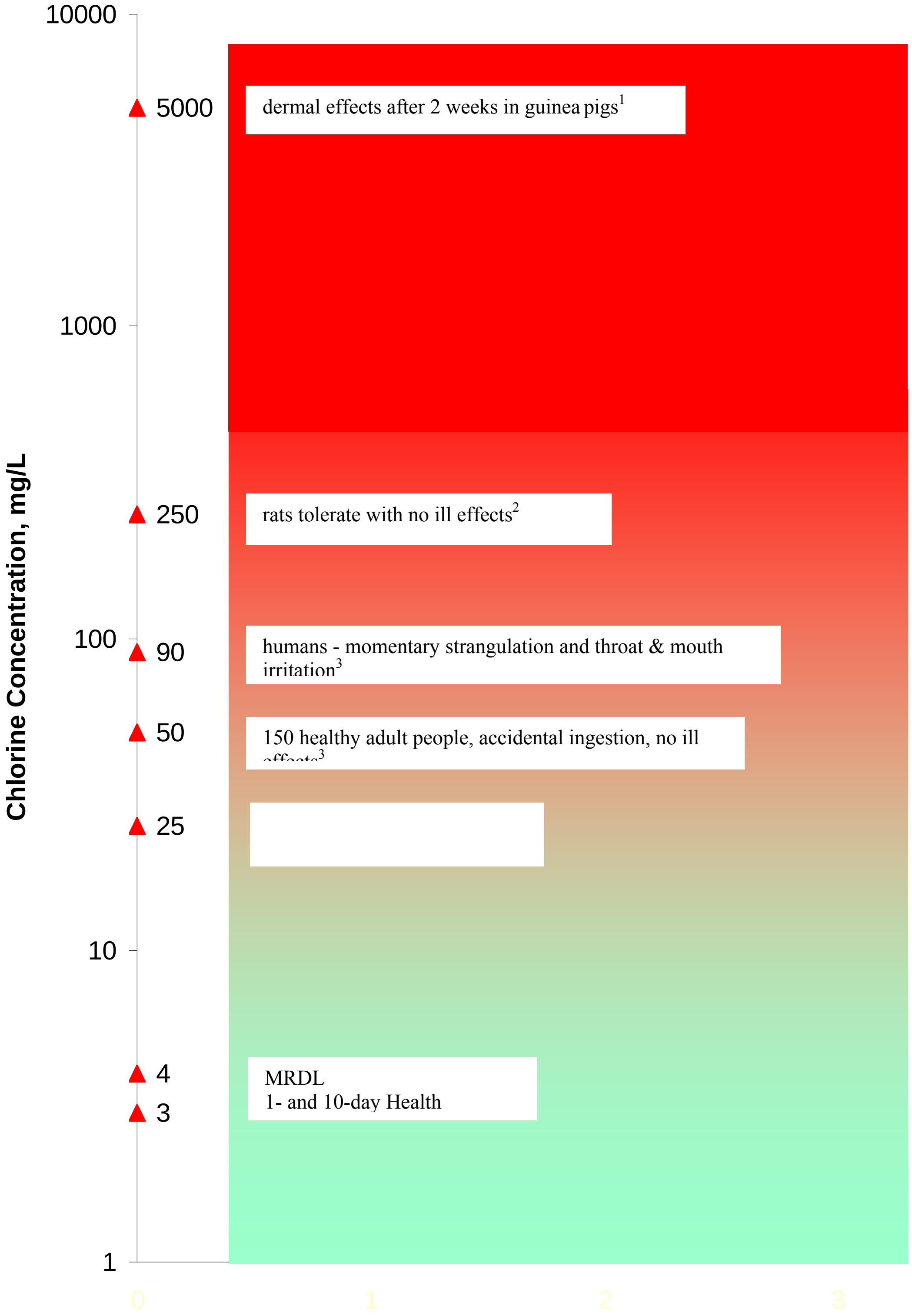

Figure 1. Chlorine Effects Levels, Exposure Limits and Recommended Immediate Action Level for Drinking Water Treatment Plants. [1]- Cotter et al., 1985; [2]- Druckrey 1968, Furukawa et al 1980, Hasegawa et al 1986 and Kurokawa et al. 1986b cited in Bull 1992; [3] – Muegge et al. 1956 cited n US EPA 1995; [4] - FR. 1994. Drinking Water; National Primary Drinking Water Regulations: Disinfectants and Disinfection Byproducts. U.S. Environmental Protection Agency. 40 CFR Parts 141 and 142. Para IX. D.July 29, 1994. 38668-38829.

whirlpool baths are >3 - <10 mg/L. The degree of ocular irritation is also a function of the chlorine species present and the pH level, with the potential for irritation being more pronounced at lower pHs.

IV. Recommended Limits for the Disinfectant Chlorine Dioxide

The following Immediate Action Levels are recommended for those systems disinfecting with chlorine dioxide:

Measured Parameter	Immediate Action Level, mg/L	Applicable to:
chlorine dioxide	2 mg/L	women of childbearing age, infants and young children
	72 mg/L	other healthy members of the population
chlorite	2 mg/L	women of childbearing age, infants and young children
	72 mg/L	other healthy members of the population
pH, free chlorine	<4.5 (low pH) >11.0 (high pH) 25 mg/L (free chlorine)	all
pH, ORP*(sample location on chlorine dioxide delivery line)	employ facility-specific limits.	all

* ORP = oxidation-reduction potential

Treatment and Monitoring Systems

Chlorine dioxide can be generated at water treatment plants by a number of processes which Gates (1998) has characterized as generally involving reaction of sodium chlorite ($NaClO_2$) or chlorate solutions with oxidizing agents such as: gaseous or aqueous chlorine alone; a mineral acid by itself or with chlorine; or acid in combination with a hypochlorite salt solution.

Six water treatment plants in MassDEP's Northeast Region employ chlorine dioxide as a disinfectant. The operational practices at these plants have been summarized by

Zessoules (2008, Appendix A). To paraphrase his observations, three means of generating chlorine dioxide are utilized onsite at these facilities:

i. a two chemical process involving combining chlorine gas and sodium chlorite;

ii. a three-chemical process involving the combination of sodium chlorite, sodium hypochlorite and sulfuric acid; and

iii. a three chemical process involving a commercial preparation called Purate (sodium chlorate and hydrogen peroxide) plus sulfuric acid.

A conceptualized process flow diagram for drinking water disinfection using chlorine dioxide through drinking water plants from source water through delivery to the point of entry into the distribution system is shown in Figure 2. Only the chlorine dioxide disinfection portions of the treatment process are indicated along with representation of monitoring that is conducted on the system.

Monitoring is performed for two reasons: to determine compliance with state drinking water standards; and for monitoring the operational status of the water treatment system.

Background and Existing Drinking Water Standards

Chlorine dioxide in water is unstable and readily dissociates primarily into chlorite and chloride, secondarily into chlorate (US EPA 2000b).

$$ClO_2 \rightarrow ClO_2^- + ClO_3^{--} + Cl^-$$

There is also interconversion between forms in the water and the human gut. Because of this chemistry and similarities in toxicities, chlorine dioxide and chlorite have been reviewed together by other groups such as the US EPA (2000b) and ATSDR (2004).

A federal drinking water standard (MRDL) for chlorine dioxide of 0.8 mg/L was established by US EPA in its Stage 1 Disinfectants and Disinfectants Byproducts Rule in 1998. The MCL for the byproduct, chlorite is 1.0 mg/L. The 1- and 10-day Health Advisory (HA) values for both chlorine dioxide and chlorite are 0.84 mg/L and are set to protect the most sensitive group, children.

The critical study that is the basis of all of the above criteria for both chlorite and chlorine dioxide is a two-generation developmental study in rats exposed to chlorite (CMA, 1996).

Sampling and Compliance With Chlorine Dioxide MRDL and Chlorite MCL

Sampling for compliance with the chlorine dioxide MRDL and chlorite MCL is described in US EPA (1998) and consists of daily sample monitoring at the entrance to the distribution system. In addition, for chlorite, a monthly sampling of three samples on the same day at designated locations within the distribution system must also be taken.

Compliance with the MCL for chlorite is determined as follows. If the daily sample result at the entrance of the distribution system is greater than the MCL of 1.0 mg/L for chlorite, then 3 samples must be taken the next day at 3 designated locations within the distribution system. The system will be out of compliance with the MCL if the arithmetic average of any three sample set within the distribution system is greater than the MCL.

Compliance with the chlorine dioxide MRDL is somewhat more complicated. There are acute violations and non-acute violations of the MRDL. If the daily sample result at the entrance to the distribution system is greater than the MRDL, then the system must sample at three designated locations within the distribution system on the next day. If the chlorine dioxide concentration for any sample at the entrance to the distribution system is greater than the MRDL AND the result for one or more of the three samples from the distribution system taken on the following day are greater than the MRDL, the system is in acute violation of the MRDL. The system will have to take immediate corrective action to lower the occurrence of chlorine dioxide below the MRDL and issue the required acute public notification (US EPA, 1998).

Health Advisory (HA) values are non-regulatory concentrations associated with no adverse health effects from ingestion exposures for periods up to the duration associated with the particular HA (e.g., 1-day). There is therefore no required sampling regimen associated with determining compliance with the HA values. They are not immediate “DO NOT DRINK” type of values.

Compliance with the drinking water standards for chlorine dioxide and chlorite is determined differently than for other disinfectant and disinfectant byproduct chemicals because the critical health effect used for setting the standard is a developmental endpoint, rather than a chronic toxicity endpoint. Chemicals which produce developmental or reproductive toxicity generally exert their toxicity within shorter time frames than occurs with chronic toxicity. These critical windows of exposure necessitate that potential shorter-term excursions in concentrations be minimized. This is done with short duration compliance determinations such as exists for chlorine dioxide. However, this monitoring is not of sufficient frequency to quickly pick up an upset condition, unless the daily grab sample coincidentally was taken at the same time or just after the start of an upset condition

Operational status monitoring is performed to document that the water quality is being maintained within defined limits and that treatment systems are functioning correctly. Ideally, online chlorine dioxide monitors could be used to determine if chlorine dioxide concentrations exceed any acute health-based concentration limits when an upset event occurs. However, only one of the six facilities in northeastern Massachusetts presently employing chlorine dioxide disinfection has an online chlorine dioxide monitor. We therefore are identifying limits for several operational parameters monitored continuously in these systems as alternatives to online chlorine dioxide monitoring. Because of the rapid conversion of chlorine dioxide to chlorite and chlorate, chlorite concentrations would be an alternative indicator of upset conditions. While real-time chlorite monitors exist, none of these six facilities reportedly has online chlorite monitors.

Other operational status online monitoring instruments employed at all facilities include pH and oxidation/reduction potential meters on the chlorine dioxide feed line and pH and free (or residual) chlorine online meters on finished water at the point of entry into the distribution system. The readings provided by these instruments provide good indications of upset conditions involving chlorine dioxide and its precursors. Table 1 shows each of the process chemicals that are being used to generate chlorine dioxide at public water supplies in northeastern Massachusetts and their relationships to each of these three indicators.

Table 1. Real-Time Monitoring for Chlorine Dioxide Generation Process Chemical Upset Conditions

ClO_2 Preparation Method	Chemical	Formula	Possible Real-Time Indicator and Relationship to Chemical Concentration		
			pH	**ORP***	**chlorine**
A. “Purate”	sodium chlorate	$NaClO_3$	1/α	α	α
	hydrogen peroxide	H_2O_2		α	
	sulfuric acid	H_2SO_4	1/α	α	
B. Two-Chemical	chlorine gas	Cl_2	1/α	α	α
	sodium chlorite	$NaClO_2$		α	α
C. Three-Chemical	sodium chlorite	$NaClO_2$			α
	sodium hypochlorite	$NaClO$	1/α	α	α
	sulfuric acid	H_2SO_4	1/α	α	

Key: α means proportional to; 1/ α means inversely proportional to;
* ORP = oxidation-reduction potential

For meters located on the chlorine dioxide feed lines, optimal operating ranges for pH and ORP are used by some of the plants to indicate when the chlorine dioxide generation process is functioning normally. When values for either pH or ORP go beyond the optimal operating range, this is an indication of some problem with the relative amounts of inputs of precursor chemicals. For online pH and chlorine meters at the point of entry to the distribution system, the health-based indicator values for pH and chlorine residual provided elsewhere in this guidance should provide additional checks on upset conditions.

Identification of Health-Based Immediate Action Levels for Chlorine Dioxide and Chlorite

For those water systems disinfecting with chlorine dioxide and having real-time monitoring capabilities for chlorine dioxide and/or chlorite, health-based acute exposure limits may be used as direct indicators of potential toxicity associated with "upset" concentrations of these chemicals.

The derivation of acute exposure limits should ideally be based on the acute toxicity database for these chemicals. The limited acute toxicity information available for chlorine dioxide and chlorite has been summarized in the US EPA and ATSDR toxicological reviews noted above. Ingestion of high concentrations of chlorine dioxide or chlorite could produce irritation in the mouth, esophagus, or stomach. The chlorine dioxide data however are not sufficiently extensive to use for setting an Immediate Action Level, as most of the observations concern mortality.

Since chlorine dioxide is rapidly converted to chlorite in water systems and there appears to be more extensive literature on chlorite toxicity, the chlorite database was used to identify a health-based acute exposure limit that may apply to both chlorite and chlorine dioxide. This approach is consistent with EPA's approach for deriving the RfD, the HA and MRDL for chlorine dioxide.

The critical toxicological endpoints identified from the literature reviews for chlorite are neurodevelopmental and neurobehavioral effects seen in animals from exposures before birth or during early development after birth. We therefore can look to the developmental and reproductive study results to provide a basis for setting an acute exposure limit for this chemical.

The 2-generation rat study used as the basis for development of US EPA's NOAEL[1] (CMA, 1996) included the finite phases of the animal's lifecycle when they would be susceptible to developmental or reproductive effects. From the chlorite study results, it is not possible to determine how long of an exposure during pre- or post-natal development is needed to produce adverse effects. We therefore make the conservative assumption for this derivation that any short duration exposure level at which effects have been seen in humans or animals during the developmental period could be capable of producing those effects in humans with only very short-term (e.g., hours) exposures such as could occur after an upset condition at a water treatment plant.

A study LOAEL[1] of 6 mg/kg/d chlorite was identified from the CMA (1996) rat study. Our objective is to protect customers of the water companies from any significant adverse health effects as a result of short-term exposures to chlorine dioxide or chlorite as a result of treatment plant upset conditions. We therefore chose a starting point based upon observed neurobehavioral effects (LOAEL) associated with exposures (in animals) during prenatal development. This number was the basis for the derivation of a "do not drink" action level for water treatment plants.

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[1] NOAEL – no observed adverse effects level; LOAEL – lowest observed adverse effects level

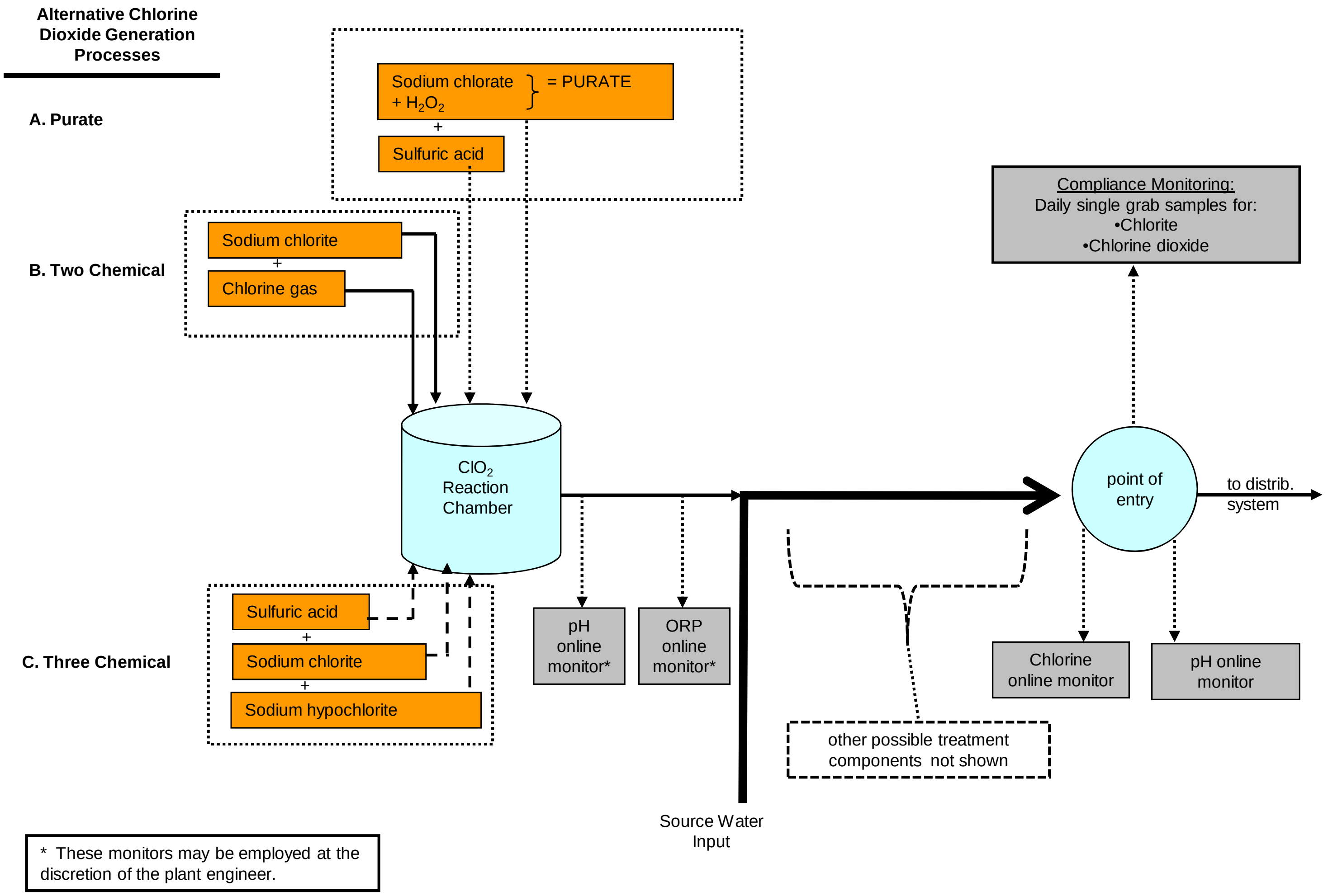

Figure 2. Hypothetical Chlorine Dioxide Generation and Monitoring in a Water Treatment Plant

An Immediate Action Level can be derived from the LOAEL of 6 mg/kg/d by dividing the value by default uncertainty factors of: a) 10 for interspecies extrapolation of the results from rats to humans, and b) 10 for sensitive individuals within the population. This operation gives an acute dose of 0.06 mg/kg/d.

This value can be translated into an equivalent concentration in drinking water of **2 mg/L** by using the default adult exposure parameters of 70 kg body weight and 2 L/d drinking water ingestion.

We considered employing either an additional uncertainty factor of 2 in the derivation of the RfD or using children's exposure parameters for the translation of the RfD to the drinking water concentration to reflect the greater exposures that children experience relative to adults. However, US EPA provided their perspective on these additional considerations with the final rule: "*The MCLG and MRDLG presented for chlorite and chlorine dioxide*" (0.8 mg/L for each) "*are considered to be protective of susceptible groups, including children, given that the RfD is based on a NOAEL derived from developmental testing, which includes a two-generation reproductive study. A two-generation reproductive study evaluates the effects of chemicals on the entire developmental and reproductive life of the organism. Additionally, current methods for developing RfDs are designed to be protective for sensitive populations. In the case of chlorite and chlorine dioxide a factor of 10 was used to account for variability between the average human response and the response of more sensitive individuals. In addition, the important exposure is that of the pregnant and lactating female and the nursing pup. The 2 liter per day water consumption and the 70 kg body weight assumptions are viewed as adequately protective of all groups.*" (US EPA, 1998).

We therefore choose a chlorite concentration of 2 mg/L as an upper do not use/do not drink value applicable to pregnant women, infants and young children. If faced with the need to issue emergency notifications to the public in the face of upset conditions with systems employing chlorine dioxide for disinfection, water suppliers may wish to direct their notification to the identified sensitive subgroups: pregnant women (prudent to include all women of child-bearing age to capture those who may unknowingly be pregnant), infants and young children.

In order to provide guidance to adults, the work of the World Health Organization (WHO, 2005) provides a useful starting point. They concluded from their review of the toxicity of chlorine dioxide and chlorite that "humans are probably not sensitive to the concentrations of chlorite that are likely to be found in water disinfected with chlorine dioxide. Some safety factor is present in these data, because it is unlikely that concentrations of chlorite would exceed 1 mg/L". They also noted that the studies "provide little information relative to the actual margin of safety that exists between those concentrations seen or administered and concentrations that would lead to clear adverse effects. Consequently, these studies do not imply that the concentrations of chlorite in drinking-water should be without limits". Highest one-time exposure concentrations to chlorite in healthy human volunteers of from 5-24 mg/L have not been associated with any demonstrable adverse clinical effects on hematology and blood chemistry (see

Lubbers et al. 1981,1982, 1984; Lubbers and Bianchine 1984; all cited in (WHO, 2005). Another perspective on chlorine dioxide and chlorite acute toxicity is provided from chlorine dioxide's use as a water disinfectant in tablet form for campers, hikers and those needing to make potable water from natural water sources. These tablets generally contain 6.4% sodium chlorite and 1% sodium dichloroisocyanurate dihydrate. Users are instructed to add the tablet to one liter of water. The manufacturer of the tablets indicates that they generate solutions with from 3-5 mg/L chlorine dioxide and a small amount of unreacted chlorite ion[2]. The labels carry no warnings about potential adverse health effects, and presumably most users are healthy individuals engaged in outdoor activities. In light of this widespread use and the human exposure studies, an upper limit of something in the range of 5 mg/L on chlorite exposures for healthy adults would seem to be too conservative for a do not drink action level. Since the highest exposure level reported with no adverse effects was 24 mg/L, this level might serve as an upper limit do not drink level for healthy adults. Alternatively, the standard uncertainty factor of 10 could be applied to this NOAEL to extrapolate it to a LOAEL to give a concentration of 240 mg/L (using concentrations, rather than doses as a mathematical shortcut for these calculations). This value seems high. We recommend the alternative application of an uncertainty factor of 3 instead of 10 to give an upper limit of 72 mg/L to indicate when notices should be issued to also warn healthy adults not to drink the water.

Statistical Reality Check

To provide some perspective on the feasibility of using the health-based value in the context of a typical water treatment plant utilizing chlorine dioxide disinfection, a statistical approach was used to identify "outlier" concentrations of chlorite and chloride dioxide that might be indicative of an upset condition. The approach used is borrowed from the industrial process control literature and is used to identify concentrations that fall outside the range of normal operating conditions. Daily monitoring data over a period of one year from six public water supplies in Massachusetts that use chlorine dioxide disinfection were used for this evaluation. These data were summarized in a database that contained over 1400 daily concentrations each for chlorine dioxide and chlorite. The distributions of values were described using standard statistics of mean and standard deviation. In general, these concentrations were lognormally distributed. Most values were quite low, with chlorine dioxide concentrations lower than chlorite concentrations, and there were many non-detect values (i.e., approximately 13% of the chlorite values and 66% of the chlorine dioxide values were "ND" or censored).
Both Kaplan-Meier survival analysis and Maximum Likelihood Estimation (MLE) statistical methods were employed to better characterize the distributional characteristics of these heavily censored data sets. The Kaplan-Meier method is a non-parametric approach that is recommended with data sets containing less than 50% censored data. The MLE method is a parametric method that is recommended with data sets containing between 50-80% censored data. Based on these recommendations, the summary statistics describing the distributions of chlorite and chlorine dioxide for both of these chemicals

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[2] Personal Communication 12/28/07 from Mr. Barry Speronello, Research Fellow, BASF Catalysts LLC.

were determined using the Kaplan-Meier method (using Statistica® software) for the chlorite data and the MLE method (using Minitab® software) for the chlorine dioxide data (Table 2).

Table 2. Summary Statistics for Chlorine Dioxide Data

PARAMETER	Chlorite	Chlorine Dioxide
Total # data points	1454	1482
Percent Censored Data	13%	66%
Mean	*---	0.072 mg/L
Standard Deviation	*---	0.077 mg/L
Median	0.14 mg/L	0.049 mg/L
First Quartile	0.33 mg/L	0.027 mg/L
Third Quartile	0.1 mg/L	0.089 mg/L
Interquartile Range	0.22 mg/L	0.061 mg/L

* The mean and standard deviation using the Kaplan-Meier method may not be useful measures due to the skewness of most survival data and thus they were not calculated.

A variety of definitions of "outlier" concentrations were identified from the process control literature (included in Table 3). Using the information in Table 2 together with these definitions, a series of outlier concentrations for each chemical (on the high end of each distribution) were determined (Table 3).

The estimated outlier concentrations are all well within the typical range of chlorite and chlorine dioxide concentrations seen at normally operating chlorine dioxide treatment plants. They are also all below the respective MCL/MRDL for chlorite/chlorine dioxide as well as the acute exposure limit developed in the above sections for these compounds. Several factors could explain why these calculated "outlier" values were not so extreme. The disinfection process with chlorine dioxide is fairly well-controlled and thus the database of monitored concentrations may not provide a good basis for identifying a usable outlier. This particular database had a very high percentage of censored data, thus resulting in a highly skewed database and many very low concentrations. Finally, it is very possible that the lognormal curve fit to the data by MLE did not provide a good fit as a result of the highly skewed data set.

The health-based value derived above was compared to the calculated "outlier" concentrations presented in Table 3. There was concern that the value of 2 mg/L developed for sensitive subpopulations was perhaps too low as it was not too far off in magnitude from the MCL and MRDL for these chemicals. However, the above exercise supports the observation that there is not much variation in a normally operating chlorine dioxide treatment process. We therefore conclude that 2 mg/L is a reasonable health-based level for identifying potential "upset" conditions at facilities employing chlorine dioxide treatment.

Table 3. Calculated Outliers

Type	Mathematical definition	Outlier Concentration (mg/L)		Probability of Getting (%)	
		Chlorite	Chlorine dioxide	Chlorite	Chlorine dioxide
Outlier	> or < ±2σ from the mean	-----	0.16	-----	8.8
Mild outlier	$< Q_{0.25} - 1.5$ * Interquartile range(IQR) or **> $Q_{0.75}$ +1.5 * IQR** (Occurring about 1 out of 150 values in a normally distributed population)	0.43	0.18	-----	6.8
Extreme outlier	$< Q_{0.25} - 3$*IQR or **> $Q_{0.75}$ + 3*IQR** (occurring about 1 in 425,000 values)	0.76	0.27	-----	2.5

Summary of Monitoring Parameters for Chlorine Dioxide

Table 4 summarizes the alternative Acute Exposure Limits discussed above for different indicator chemicals associated with the use of chlorine dioxide for disinfection of drinking water.

Table 4. Immediate Action Levels for Chlorine Dioxide Disinfection-Associated Parameters

Measurement	Immediate Action Level, mg/L	Applicable to:
chlorine dioxide	2 mg/L	women of childbearing age, infants and young children
	72 mg/L	other healthy members of the population
chlorite	2 mg/L	women of childbearing age, infants and young children
	72 mg/L	other healthy members of the population
pH residual chlorine	<4.5 (low pH) >11.0 (high pH) 25 mg/L (free Cl)	all
pH ORP*(sample location on chlorine dioxide delivery line)	employ facility-specific limits	all

* ORP = oxidation-reduction potential

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APPENDIX A

Chlorine Dioxide Disinfection Practices at Drinking Water Treatment Plants in MassDEP's Northeast Region

From: Zessoules, Nicholas (DEP)
Sent: Monday, July 28, 2008 8:38 AM
To: Hutcheson, Michael (DEP)
Subject: FW: NERO Chlorine Dioxide Information

Please find some information related to the monitoring of chlorine dioxide in the message below. I am providing this as discussed during the meeting with Paul Niman and others on emergency chemical levels in May.

Please let me know if you have any questions.

From: Zessoules, Nicholas (DEP)
Sent: Friday, July 25, 2008 10:46 AM
To: Niman, Paul (DEP)
Subject: NERO Chlorine Dioxide Information

Below are my notes on chlorine dioxide for consideration. I investigated chlorine dioxide as discussed during the May meeting.

The primary focus of the discussion was on monitoring, To summarize, monitoring practices in NERO consist of the following:

- Monitoring of the effluent for chlorine dioxide and chlorite using grab samples, to comply with the Stage 1 requirements
- Monitoring of the chlorine dioxide solution stream for pH and ORP
- On-line chlorine dioxide monitoring at one plant only

Further, chlorine dioxide at all NERO regulated facilities is followed by GAC filtration and point-of-entry monitoring for chlorine and pH.

My sense is that monitoring for "gross" releases of any constituent used to form chlorine dioxide is in place now, but that monitoring for chlorine dioxide itself and chlorite is limited to process control monitoring and daily grab samples.

I can discuss at greater length at the meeting.

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Chlorine Dioxide Notes

The following systems in the Northeast region use chlorine dioxide:

- Ipswich
- Lawrence
- Lowell
- Lynn
- Methuen
- Tewksbury

All of the above are surface water treatment plants. Five of six of the plants are conventional filtration plants, with Lynn a direct filtration plant. All of the plants have granular activated carbon media filters after chlorine dioxide is added. All of the plants use the chlorine dioxide as a pre-oxidant. Three of the plants (Ipswich, Lowell, and Lynn) monitor chlorine dioxide to demonstrate primary disinfection. All of the plants also add chlorine after filtration, with five of the six using the post-filtration chlorination as part of its primary disinfection.

Generation process:

Chlorine dioxide is generated by either a two-chemical or three-chemical process. The standard two-chemical process, which is used by Lynn, involves combining chlorine gas and sodium chlorite. The three-chemical process, used by four of the other water suppliers, involves combining sodium chlorite, sodium hypochlorite, and sulfuric acid. All of these include a reaction chamber that allows the chemical reaction to convert the chlorite into chlorine dioxide to occur.

Sodium chlorite is common to the most common methods of generation in use. Sodium chlorite is supplied in both 25 percent and 38 percent solutions. Sodium chlorite is described in an MSDS as a pale green liquid with a fain bleach odor. Physical and chemical properties of a 25% solution are:

- pH: 12.5 to 13
- Specific Gravity: 1.24
- Boiling point: 106 C
- Melting point: -9 C
- Solubility: Miscible in water

Ipswich uses a two-chemical process; however, their process uses Purate and sulfuric acid, to form chlorine dioxide. A description of Purate describes the chemical as a clear, faintly blue, odorless liquid, composed of sodium chlorate and hydrogen peroxide. Its chemical and physical properties are:

- pH: 1.7
- Specific Gravity: 1.37
- Boiling point: 104 C
- Melting point: Not available
- Solubility: Not applicable

There are two types of process configurations used. One is an intermittent, or a batch, process, used in Lynn and Lowell, which involves storing chlorine dioxide solution in a holding tank after generation, with the solution then pumped into the water supply as needed. The other configuration is a continuous process, used in Ipswich and Tewksbury, where the chlorine dioxide is added to the water supply as it is generated.

Monitoring:

All facilities are required to monitor chlorine dioxide once a day at the point of entry, with facilities that are using chlorine dioxide for primary disinfection also monitoring the chlorine dioxide levels elsewhere in the plant. Only Lowell has on-line monitors for measuring chlorine dioxide; they monitor chlorine dioxide immediately after addition and prior to flocculation. At the other treatment plants, chlorine dioxide is measured by collecting grab samples once a day and analyzing the samples in the treatment plant's lab. A representative from International Dioxide indicated that on-line monitoring of chlorine dioxide is now more common, and indicated that several suppliers of chlorine dioxide monitors now exist. Discussions with Lowell and an out-of-state water supplier indicate that these monitors are accurate. In a single comparison, Lowell noted a slight difference between the monitor and a grab sample analyzed in the lab which Lowell attributed to a decay on dioxide level because of a time delay.

All facilities are required to monitor chlorite at the point of entry. None of the facilities have on-line monitoring for chlorite. All monitor chlorite by collecting grab samples and analyze the chlorite concentrations in the on-site lab.

The methodology for analyzing chlorine dioxide and chlorite involves titration, which generally requires more experienced personnel. The analysis process for one sample has been reported by several operators to take approximately 25 minutes.

All of the plants except Lynn also measure chlorine dioxide generator efficiency. The generator efficiency, as described in literature and Standard Methods, is a measure of the amount of chlorine dioxide produced as a percent of the dioxide and the chlorite and chlorate levels in the final solution. It should be noted that the value does not consider excess chlorine, which can be generated by the process. Ipswich and Lowell have on-line instruments for monitoring generator efficiency.

Several of the plants have pH and ORP monitors on the chlorine dioxide feed line. These monitors can detect changes in the chlorine dioxide solution. Operators have reported the normal pH has a range of approximately 0.5 standard units. The target and actual pH values reported by operators are generally similar. At Lowell, the range was defined as 2.5 to 3.0, which is the same target range as Lynn. For Lawrence, the SOP defines the optimal pH range as between 2.6 and 2.9. For ORP, the Lawrence SOP notes that the ORP should be between 1200 and 1400, with a value of over 1500 "undesirable". The SOP also notes that:

- ORP increases directly with increasing hypochlorite
- ORP increases with drops in pH
- Sodium chlorite decreases will decrease the pH

In all cases, on-line monitoring at the entry point or before includes monitoring for pH and chlorine.

Physical Controls:

The physical controls for the chlorine dioxide systems vary and depend in part on the type of feed system. Lowell uses normally-closed solenoid valves, energized when the dioxide generator is energized, on the chemical feed lines. Such devices provide positive shut off when the facility is not in use. Other controls include flow pacing and use of vacuum systems.

Treatment Removal Efficiency:

As noted above, all of the facilities that use chlorine dioxide in the Northeast region have treatment to include GAC media filters downstream of point where the chlorine dioxide is applied. The data on chlorine dioxide removal efficiency of the treatment process is limited. At Lowell, which uses conventional filtration with a GAC polishing filter, the available information indicates that chlorine dioxide levels of up to 0.21 mg/l are completely removed through the treatment process. At Lynn, which uses direct filtration with GAC media after coagulation with alum and pH adjustment, the available information indicates that the direct filtration process reduced chlorine dioxide levels about 0.23 mg/l, equal to a 66% removal rate, on average, with chlorine dioxide levels in the finished water of 0.12 mg/l on average and a maximum of 0.3 mg/l, or approximately 38% of the MRDL.

There is no information readily available from the facilities on chlorite removal efficiency. A single sample set from Lowell indicates that any removal occurs in the filtration process (sand and GAC), with samples collected after filtration showing a 0.7 mg/l reduction in chlorite level as compared to a sample collected prior to filtration.

Process Experience

No one I contacted was aware of any incidents involving over-feeds or releases of any of the constituent chemicals into the drinking water from a chlorine dioxide system.