

Human health risk assessment – chlorate in drinking water

Summary

Chlorate is a breakdown product of sodium hypochlorite, which is commonly used in the disinfection of drinking water. Chlorate is a public health concern due to its potential adverse effects on human health. Drinking water is the main source of exposure to chlorate, followed by food. There is currently no Australian Drinking Water Guideline (ADWG) for chlorate.

Correct management of stored hypochlorite provides the best option for drinking water service providers to reduce the formation of chlorate.

The dose of sodium hypochlorite used should not be reduced in order to reduce chlorate levels if this has the effect of reducing the concentration of free chlorine during the treatment process, as this will compromise disinfection effectiveness.

Once chlorate has entered the reticulation system, there are no options to reduce community exposure other than via a 'do not consume' alert for long-term exceedances.

Background

This risk assessment has been prepared to assist Queensland drinking water service providers and regulatory agencies to respond to chlorate detections in treated drinking water.

Chlorate (ClO_3^-) occurs as a breakdown product of sodium hypochlorite (NaOCl) solution during manufacture, transport and storage of the product. As chlorate forms, the available chlorine concentration decreases and higher doses of sodium hypochlorite must be added to the water to achieve the desired free chlorine residual concentration. Consequently, increased amounts of chlorate may be added to drinking water.

Chlorate is a potential health hazard in drinking water because, at concentrations well above what is typically found, it can cause damage to red blood cells and disturb thyroid function, and may cause liver and kidney damage.

There is no Australian drinking water guideline for chlorate. Values of 0.8 and 0.3 mg/L were suggested in the 2011 review of the Australian Drinking Water Guidelines, but no



determination was able to be made (NHMRC 2011). Guideline values in other jurisdictions range from 0.21 to 1 mg/L (Table 1).

Table 1. Guideline values for chlorate in other jurisdictions.

Jurisdiction		Value (mg/L)	Source
Canada	Maximum Acceptable Concentration	1*	(Health Canada 2008)
New Zealand	Guideline	0.8	(Ministry of Health 2017)
WHO	Guideline	0.7	(WHO 2011)
USEPA	Health Reference Level	0.21**	(Alfredo et al. 2014)
California EPA	Notification level	0.8	(Alfredo et al. 2014)
	Public Health Protective Concentration (C)	0.21**	

*Based on drinking water intake of 1.5 L/day. At a drinking water intake of 2 L/day this would be 0.8 (rounded from 0.84); this also includes a Safety Factor=1000

**C = 30 mg/kg-day x 70 kg x 0.2/1,000 x 2 L/day = 0.21 mg/L

Hazard Assessment

The acute toxicity of chlorate is well understood, due to its use as a pesticide. An acute lethal dose as a single dose for an adult is 5-10 g, and for a child is 2 g. Symptoms of oral ingestion of an acute dose include abdominal pain, nausea, vomiting, diarrhoea, pallor, cyanosis (blueness of the skin), shortness of breath, unconsciousness and collapse (USEPA 2016).

In drinking water, sub-chronic studies suggest that chlorate has a no observed adverse effect level¹ (NOAEL) of 36 µg/kg body weight (bw) per day, based on the highest dose in a 12-week study in human volunteers (2.4 mg/L in 0.5 L of water). Slight changes in group mean serum urea nitrogen and mean corpuscular haemoglobin were not considered physiologically significant, as values remained within the normal range for each parameter (Lubbers et al. 1981). A 90-day study in rats identified a NOAEL of 30 mg/kg bw per day based on thyroid gland colloidal depletion at the next dose of 100 mg/kg bw per

¹ In this context the NOAEL is the highest dose of a chemical at which there were no adverse effects observed in experimental studies.

day(McCauley et al.1995). Applying an uncertainty factor of 1000 to this NOAEL (10 each for intra- and inter-species variation and 10 for the short duration of the study) results in a tolerable daily intake² (TDI) of 30 µg/kg bw per day, which is supported by the human volunteer studies(WHO 2005).

The European Food Safety Authority (EFSA) determined a TDI of 3 µg/kg bw per day by 'read across' from a TDI of 0.3 µg/kg bw per day for the higher potency perchlorate, for the critical effect of inhibition of iodine uptake in the thyroid (EFSA 2015). Perchlorate (ClO₄⁻) can also be formed during the decomposition of sodium hypochlorite but perchlorate is not usually monitored in Australian drinking water.

An alternative TDI has been proposed by the Joint FAO/WHO Expert Committee on Food Additives (JECFA 2008) using the benchmark dose (BMD) approach³ to determine a point of departure from an animal study (NTP 2005) in which F344/N rats exposed to chlorate in drinking water for two years showed increased thyroid gland follicular cell carcinoma in males and thyroid gland follicular cell adenoma and carcinoma (combined) in both males and females. The TDI of 0–0.01 mg/kg bw for chlorate was calculated on the basis of the BMDL₁₀⁴of 1.1 mg/kg bw per day, applying a safety factor of 10 to allow for intraspecies variability and an additional safety factor of 10 to allow for the deficiencies in the database, particularly with respect to the investigation of possible neurodevelopmental effects(JECFA 2008).

Using the NTP (2005) study BMD₁₀ as the departure point, a water quality guideline value of 0.3 mg/L can be calculated (**Equation 1**).

$$\frac{0.01 \frac{mg}{kgbw} \times 70 kg \times 0.8}{2 L} = 0.28 \text{ rounded to } 0.3 \text{ mg/L} \quad \text{Equation 1}$$

Where:

0.01 is the TDI for chlorate based on BMD₁₀ in a study of F344/N rats

70 kg is the default body weight for an adult

0.8 is the fraction of intake attributable to drinking water

2 L is the average daily intake of water

² Tolerable daily intake is the amount of a substance in air, food or drinking water that can be taken in daily over a lifetime without appreciable health risk.

³ Benchmark dose is the dose that corresponds to a specific change in an adverse response compared to the response in unexposed subjects. While similar to a NOAEL, it uses more biological information and is more mathematically precise.

⁴ BMDL₁₀ is the dose where the change in response is likely to be less than 10%

Based on a TDI of 30 µg/kg bw per day, a drinking water guideline value of 0.8 mg/L is calculated (Equation 2).

$$\frac{0.03 \frac{mg}{kgbw} \times 70 kg \times 0.8}{2 L} = 0.84 \text{ rounded to } 0.8 \text{ mg/L} \quad \text{Equation 2}$$

Where:

0.03 mg/kg bw per day is the TDI based on a NOAEL from a 90-day study in rats

70 kg is the default body weight for an adult

0.8 is the fraction of intake attributable to drinking water

2 L is the average daily intake of water

As rats are considered to be highly sensitive to the effects of agents that disrupt thyroid hormone homeostasis (EFSA 2015), it is difficult to justify accepting the lower result based on animal data, when there is a result which is supported by human data. Given the range of international guidelines for chlorate, it is not clear that 0.3 mg/l is significantly more protective of human health than 0.8 mg/L.

Based on the above considerations, 0.8 mg/L is the preferred guideline value for drinking water in Queensland.

Exposure Assessment

Sodium chlorate is approved for use in Queensland as a defoliant on cotton crops.

Potassium chlorate is also an active ingredient in smoke generator fumigants. Chlorate can occur in food from the use of chlorinated water for food processing and the disinfection of food processing equipment. In a survey of dietary exposure in Europe, across all age classes and vulnerable groups, the main average contributor to dietary exposure was drinking water (EFSA 2015). The highest exposure occurred in infants (6.6 µg/kg bw per day (upper bound)).

The difference between guideline values 0.8 and 0.2 mg/L are largely the result of assumptions on the contribution of drinking water to chlorate exposure (80% and 20% respectively). The WHO guideline of 0.7 mg/L assumes 80% contribution from drinking water, but with 60 kg body weight rather than 70 kg (WHO 2005). The Australian drinking water guideline for chlorite, which also occurs as a decomposition product in hypochlorite, attributes 80% of total daily intake to the consumption of water (based on occasional use of chlorite in the food industry) (NHMRC 2011). A similar argument has been applied for chlorate.

Risk Characterisation

Elevated concentrations of chlorate, particularly if significantly and consistently above 0.8 mg/L, is a concern. While there is no definitive evidence to support any given period of exposure, the duration of the human health study (Lubbers et al. 1981), which was 12 weeks, should not be exceeded.

Uncertainties

There is a lack of human data on the inhibition, by chlorate, of iodine uptake by the thyroid and its relative potency compared to perchlorate (EFSA 2015).

Although there are mixture studies of chlorate and perchlorate, there is a lack of mixture studies for chlorite plus chlorate (USEPA 2016). Therefore, additional consideration should be given to the presence of chlorate when it occurs in addition to elevated concentrations of chlorite or perchlorate.

Long-term considerations

There is no evidence that chlorate is carcinogenic in humans at exposures expected to result from drinking water.

Characterisation of ongoing risks

If persistent chlorate exceedances in a community water system are not able to be brought under control, Queensland Health could give consideration to public health surveillance for increased incidence of thyroid disease. However, thyroid disease is not an easy outcome to measure. It is not a notifiable disease, and its incidence is not routinely recorded in any currently existing QH surveillance system even though it is the expected outcome from exposure to a number of environmental toxicants.

Risk Management

Control of chlorate in drinking water

In Queensland the main mechanism for chlorate formation in drinking water is via the breakdown of liquid sodium hypochlorite. This transformation takes place from initial production of sodium hypochlorite and continues during transport and storage, depending on the concentration of the sodium hypochlorite solution, the pH of the solution and temperature. Other “onsite” methods of chlorine-based disinfectant production, such as

chlorine dioxide generation or production of gaseous chlorine via electrolysis of a brine solution, are much less common and generally produce much less chlorate.

Recommendations for the management of hypochlorite include the following

- Dilute stored hypochlorite on delivery
- Store hypochlorite solutions at lower temperatures
- Control the pH of stored hypochlorite solutions at pH 11-13, even after dilution
- Avoid extended storage times.

Queensland Water Directorate (qldwater) have produced a Chlorate Fate Sheet which outlines management options for hypochlorite to minimise chlorate formation (https://www.qldwater.com.au/_literature_136339/Chlorate_Fact_Sheet). For further information on the management of hypochlorite solutions see Alfredo et al., (2014) or Stanford et al.(2011). Contact the Water Unit if you are having difficulty accessing these documents.

Reduction of community exposure

If elevated concentrations of chlorate continue for some time, or are accompanied by elevated concentrations of chlorite or perchlorate, advice should be given to the community on measures to reduce exposure.

As there is no point-of-use treatment technology to remove chlorate from tap water, the only intervention option for reducing exposure once chlorate is distributed into the reticulation system is a “do not drink” alert.

Ideally, actions should be taken to bring chlorate levels in the water being supplied to the reticulation system below 0.8 mg/L as soon as possible.

Conclusion and Recommendations

The presence of chlorate in drinking water indicates a deterioration of the hypochlorite used for disinfection. Management of the hypochlorite stocks provide the best management option to reduce chlorate. Reduction in hypochlorite use to reduce chlorate should not be used if free chlorine, and hence disinfection, is compromised.

Once chlorate has entered the reticulation system, there are no options to reduce community exposure other than a ‘do not consume’ alert for long-term exceedances. This should only be considered as a last resort, when other management options have failed to reduce chlorate concentrations to an acceptable level.

References

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