

# IT WAS OK LAST MONTH: RESULTS OF A CHLORATE SURVEY

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## **ABSTRACT (500 WORDS MAXIMUM)**

In 2016, Water New Zealand published an "Interim Good Practice Guidance Note - Supply of Chlorine for Use in Drinking-Water Treatment". It provides purchasers, manufacturers and suppliers with the minimum physical, chemical and testing requirements for chlorine to meet safe limits for drinking water supplies. The Guidance Note proposes a specific impurity limit (SIL) of 2000 mg/L for chlorate in liquid hypochlorite products, because hypochlorite in solution decomposes to chlorate: a determinand with a provisional maximum acceptable value (pMAV) of 0.8 mg/L. There were concerns over the practical difficulties in supplying liquid hypochlorite products that met the SIL and whether these difficulties might result in unacceptable chlorate concentrations in reticulated drinking-water.

This paper reports the results of a limited survey of chlorate in 25 New Zealand water supply zones undertaken in 2017-18, and funded by the Ministry of Health, to help inform development of the Guidance Note. In most zones, samples were taken from each reticulation on two occasions, and also from hypochlorite dosing solutions.

Chlorate concentrations were variable. The median chlorate concentration measured in reticulated waters was 0.14 mg/L, but 6 of 47 (13%) test results exceeded the pMAV. Only one supply contained chlorate concentrations that exceeded the pMAV on both sampling occasions (1.20 and 0.97 mg/L).

The study concluded that.

- Potentially health-significant chlorate concentrations do arise in New Zealand's reticulated waters as the result of the use of hypochlorite.
- Chlorate concentrations in reticulated water and chlorinating solutions are variable. Chlorinating solutions containing chlorate concentrations less than the SIL of 2000 mg/L are less likely to be associated with chlorate concentrations exceeding 50% of the pMAV in the reticulation.
- There is evidence that chlorinating solutions prepared by electrolysis, online and as a batch product at low hypochlorite concentration, are less likely to contain chlorate at concentrations exceeding the proposed SIL.
- Manufacturers and water suppliers share responsibility for taking steps to manage the risk associated with chlorate in water supplies.
- Several steps have been identified (by other studies) for reducing the chlorate concentration in chlorinating solutions. The most important is dilution of the hypochlorite solution.
- There are implications for the Guidance Note. The frequency at which manufacturers are required to test chlorate in their product needs to be re-examined, and the survey's findings do not support raising the proposed SIL.

- Several factors can contribute to the presence of elevated chlorate (and other oxyhalides) concentrations in drinking water chlorinated using hypochlorite. Water suppliers using hypochlorite need to be aware of these factors and ensure that this risk is managed in their water safety plans. This should include adequate monitoring as a check that their preventive measures are effective.

## KEYWORDS

**Drinking water, chlorate, hypochlorite**

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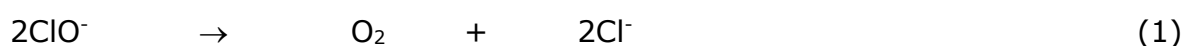
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## 1 INTRODUCTION

The most common form of disinfection in New Zealand, and throughout the world, is chlorination. In New Zealand, water supplies use both gas chlorine and solutions of hypochlorite for this purpose.

Water supplies selecting hypochlorite solutions as their chlorinating agent have to manage the problem of hypochlorite decomposition. Hypochlorite decomposition results in a gradual decrease in the free available chlorine (FAC) content of the solution (Stanford et al, 2011). This does not compromise the hypochlorite solution's disinfecting ability provided the dose rate is increased to compensate for the lower FAC concentration in the chlorinating solution.

However, hypochlorite decomposition has other consequences for the quality of the treated water. The decomposition process can follow either of two paths (equation (1) or (2)) (Standford et al, 2011):

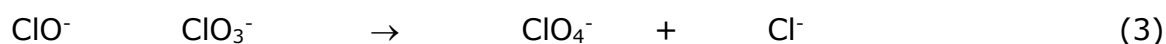


or



The second of these two pathways is of potential health significance because of the formation of chlorate ( $\text{ClO}_3^-$ ). This ion has a provisional maximum acceptable value (pMAV) of 0.8 mg/L set in the *Drinking-water Standards for New Zealand* (DWSNZ) (DWSNZ, 2018).

Chlorate itself may undergo further reaction with the hypochlorite ion to form perchlorate ( $\text{ClO}_4^-$ ), as shown in equation (3).



Perchlorate does not have a maximum acceptable value (MAV) or pMAV in the current (2005) edition of the DWSNZ (revised 2018). Since the MAVs were set in the 2005 edition of the DWSNZ, the World Health Organization (WHO) has published a guideline value for perchlorate (WHO, 2017). As the MAVs in the DWSNZ closely follow the WHO guidelines, it is likely that a MAV for perchlorate will be included in the next edition of the DWSNZ.

The presence of bromide ions in the water used to manufacture the hypochlorite product or in water used to dilute the manufacturer's product leads to the formation of bromate ( $\text{BrO}_3^-$ ) (pMAV = 0.01 mg/L) (Stanford, et al, 2011). These ions are formed by a mechanism analogous to that of chlorate.

The formation rates of chlorate and perchlorate are sufficiently rapid that these contaminants form to some extent in high-concentration hypochlorite solutions before the manufacturer can provide the product to the water supplier.

Water New Zealand has published a series of good practice guides to help ensure the quality of treatment chemicals used in New Zealand's drinking waters supplies<sup>1</sup>. The series includes an "Interim Good Practice Guidance Note" (the Guidance Note) for chlorination chemicals.

The good practice guides list specific impurity limits (SIL) for contaminants that may appear in water treatment products. During the preparation of the good practice guide for chlorination products, concerns arose that the proposed SIL for chlorate in 13% sodium hypochlorite products (2000 mg/L) would be too low for manufacturers to achieve.

While the product delivered to a water supplier might contain chlorate in excess of the SIL, the important question is whether chlorate concentrations in excess of the proposed SIL are leading to potentially health significant concentrations of chlorate in finished water.

The Ministry of Health's "Priority 2 Chemical Determinands Identification Programme", undertaken during the late 1990s, showed that some water supplies contained chlorate concentrations in excess of 50% of the MAV and the MAV (Davies et al, 2001). A recent national dataset that could be used to confirm that this was still the case was unavailable. Consequently, the Ministry of Health asked ESR to undertake a limited survey to gain an understanding of chlorate concentrations in the finished waters of hypochlorite-treated supplies. The results of this survey are presented in this paper and will be used to inform the finalisation of the Guidance Note.

## **2 METHOD**

### **2.1 IDENTIFICATION OF SUPPLIES FOR SAMPLING**

To be eligible for inclusion in the survey, supplies needed to be reticulated; treated using either sodium hypochlorite or HTH (high test hypochlorite – calcium hypochlorite); and serve a population of 100 or more people. Fifty-eight water supply managers were surveyed to determine whether they manage supplies that meet these criteria. Using a standard form, they were asked for their council name, the water supply zone (zone) name and code, and the chlorinating agent used.

Of the 58 water supply managers surveyed, 12 stated that they were not using either sodium hypochlorite or HTH for disinfection. Sixteen managers replied with details showing that they had supplies that met the criteria for inclusion in the study. The information received from the suppliers was used to identify the public health units (PHU) that would be asked to collect samples in stages two and three of the project.

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<sup>1</sup> See the Water New Zealand on-line library <https://www.waternz.org.nz/library>

## **2.2 SAMPLING WATER SUPPLIES**

The PHUs with responsibility for the water supplies that met the project acceptance criteria were contacted and asked for assistance in collecting the samples. Where a PHU was unable to assist, the councils and their sub-contractors were asked to help with sample collection.

When samples were obtained from a water supply the following were requested:

- a sample of drinking-water collected from the extremity of the supply zone in question, for chlorate determination.
- a sample of the hypochlorite dosing (chlorinating) solution collected from the treatment plant (plant), for chlorate determination.
- the FAC concentration and pH of drinking-water at the point that water left the plant.
- information on the manufacturer, batch number and expiry date of the hypochlorite product that was in use as the chlorinating solution at the time of sampling.

Sample containers for both drinking-water and chlorinating solutions were provided by Eurofins ELS laboratories (Lower Hutt, New Zealand), as the analysing laboratory. These containers conformed to the laboratories ISO17025 approved sampling protocols. As a health and safety consideration, samples of the chlorinating solution (10 mL) were immediately diluted into 40 mL of deionised water that had been provided in the sample pots by the analysing laboratory. This led to a 5-fold reduction in concentration and a subsequent reduction in exposure risk should the pot have been compromised during transport to the laboratory. Samples were analysed for chlorate concentration at Eurofins ELS laboratories by ion chromatography following the USEPA 300.0 (modified) method for inorganic anions. Results were reported directly to ESR from the laboratory.

Determination of the FAC concentration and pH of the drinking water leaving the plant were recorded by the samplers. By preference, these data were taken from the in-line monitoring systems at the plant. If these in-line systems were not functioning, or the plant did not have them installed, FAC was determined using a portable FAC meter and pH was determined with a portable pH meter. Information regarding the manufacturer of the hypochlorite product in use at each plant, its batch number and expiry date were recorded on the same form as the FAC concentration and pH data. These data were recorded on a sample information form and submitted to ESR by e-mail.

The survey was carried out in two sampling rounds. Except for three zones, two sets of samples were collected from each participating zone. Results were received by ESR and tabulated by supply zone and sampling round.

## **3 RESULTS**

### **3.1 INTRODUCTION**

At the time of preparing for the survey, there were 689 networked supplies across New Zealand. The survey of the 58 water supply managers identified 42 water supplies that met the selection criteria stated in section 2.1. The 42 supplies identified served a population of approximately 1,056,000 people, with the bulk of this population being in the Auckland region. Of these 42 supplies, samples for chlorate analysis were received from 28 zones, serving a population of approximately 355,800 people. Three of the 28

zones served populations of fewer than 100 people and, in line with the selection criteria for this study, were removed from the analysis of results.

### 3.2 SUMMARY OF RESULTS

All 25 eligible zones were sampled in the first sampling round, while 22 were sampled in the second sampling round, giving a total of 47 analyses. Data on pH, FAC and source and age of the chlorinating agent were not provided in all cases. The information provided is summarised in Table 1.

*Table 1 Information provided on hypochlorite-treated zones included in this survey (n = 25), 2017-2018*

Parameter	Number of zones for which parameter information was provided		
	First sampling	Second sampling	Total
Number of zones	25	22	47
pH	20	18	38
FAC	21	22	43
Brand of chlorinating agent	19	8	27 <sup>a</sup>
Batch number or other identifier for chlorinating agent	13 <sup>a</sup>	8 <sup>a</sup>	21 <sup>a</sup>

<sup>a</sup> For five zones chlorine is electrically generated from sodium chloride brine and this information was not relevant

Table 2 provides summary statistics for the measured parameters: pH, FAC, chlorate in chlorinating solutions and chlorate in reticulations.

*Table 2 Summary statistics for parameters measured in hypochlorite-treat zones included in this survey (n = 25), 2017-2018*

Parameter	Summary statistics for parameter		
	First sampling	Second sampling	Total
Number of zones	25	22	47
pH, mean (range)	7.64 (6.26–9.50)	7.45 (6.39–7.9)	7.55 (6.26–9.50)
FAC, mean (range), mg/L	0.92 (0.26–1.40)	1.0 (0.44–1.54)	0.96 (0.26–1.54)
Chlorate in chlorinating solution, mean (range), mg/L	4140 (315–19,200)	6850 (685–31,400)	5410 (315–31,400)
Chlorate in reticulation, mean (range), mg/L	2.0 (0.023–42.9)	4.7 (0.022–92.1)	3.3 (0.022–92.1)
Chlorate in reticulation, median, mg/L	0.11	0.14	0.14

A US study with similar design to the current study reported a mean chlorate concentration in hypochlorite solutions from two plants of 11,100 mg/L (range 2430–14,800 mg/L); approximately twice the mean concentration found in the current study (Breytus et al., 2017). Chlorate concentrations found in finished water in the US study were in the range 0.09–0.74 mg/L (mean 0.38 mg/L).

A Spanish study of chlorate concentrations in drinking-water supplies treated with hypochlorite (n = 332) reported a mean chlorate concentration of 0.22 mg/L, with a maximum of 4.3 mg/L (Garcia-Villanova et al., 2010). In the Spanish study the chlorate levels determined in the chlorinating solutions were markedly higher than those seen in the current study, with a mean chlorate concentration in sodium hypochlorite solutions (n = 39) of 30,000 mg/L (maximum 141,000 mg/L) and a mean chlorate concentration in HTH solutions (n = 10) of 24,000 mg/L (maximum 83,000 mg/L).

In a study of the potential impact of disinfection by-products on birth anomalies in northern Italy, the mean chlorate concentration in drinking-water was 0.28 mg/L (Righi et al., 2012).

In a study in Japan, which included analysis of 10 tap water samples for chlorate, chlorate concentrations were in the range 0.034–0.14 mg/L (Asami et al., 2013).

In a study of swimming pools in Italy, much higher chlorate concentrations were reported in swimming pool water treated with sodium hypochlorite than in the reticulated water supplies used to fill the pools (Righi et al., 2014). The mean and maximum chlorate concentrations in the pools were 8.9 mg/L and 19.5 mg/L respectively. Recirculation of swimming pool water contributes to the higher chlorate concentrations.

### **3.3 RETICULATION WATER QUALITY**

Of the 47 reticulation samples obtained during the survey, nine samples (19%) contained chlorate at a concentration greater than 50% of the pMAV of 0.8 mg/L. These samples came from six zones, three of which yielded reticulation chlorate concentrations greater than 50% of the pMAV in both samples. Chlorate could be assigned as a Priority 2 determinand in the six zones in which 50% of the pMAV was exceeded.

Six (12.8%) samples from reticulations contained chlorate at concentrations exceeding the pMAV. While three of these results were only just above the pMAV (1.09, 0.97 and 1.2 mg/L), the other three exceedances were markedly greater than the pMAV (6.5, 42.9 and 92.1 mg/L). The validity of these latter three very high results is discussed in the following section. If the three very high chlorate concentrations are excluded from consideration, the mean chlorate concentration in the reticulation samples is 0.24 mg/L. Only one zone contained chlorate concentrations that exceeded the pMAV on both sampling occasions (1.20 and 0.97 mg/L).

These statistics are skewed to a degree by eight samples coming from four Auckland zones, all of which receive the same treated water. The chlorate concentrations in all the Auckland zones are all less than 50% of the pMAV, at similar, low levels, except the concentrations in one zone. Both samples from this zone contained chlorate at a concentration of ca. 0.2 mg/L which, although well below 50% of the pMAV, was greater than the chlorate concentration in the other zones by a factor between five and ten.

If the results from the four Auckland zones are considered to be from multiple samples from one large zone, and the total number of results in the survey is adjusted to 41 (47 less the six results from three of the Auckland zones) the statistics change to 22% of samples exceeding 50% of the pMAV and 15% exceeding the pMAV.

### 3.3.1 VERY HIGH RETICULATION CHLORATE CONCENTRATIONS

The very high chlorate concentrations reported in three reticulated waters are left in the study's dataset, but have to be treated with caution. While the laboratory confirmed its reported results, discussions with DWAs about the operation of the three zones concerned provided no reason to expect such high concentrations.

Table 3 provides the available information for the three zones from which one reticulation sample with a very high chlorate concentration was obtained. The three zones were sampled in both sampling rounds, but the very high chlorate concentrations were only found at one sampling from each zone.

*Table 3 Information on zones with very high chlorate concentrations*

Parameter	Zone A	Zone B	Zone C	Survey mean
Reticulation chlorate, first sampling, mg/L	42.9	6.5	92.1	2.9
Reticulation chlorate, second sampling, mg/L	0.50	0.096	0.081	
pH, first sampling	7.50	6.39	NR	7.55
pH, second sampling	7.25	6.26	NR	
FAC, first sampling	1.1	1.3	0.51	1.1
FAC, second sampling	1.3	1.0	NR	
Chlorate in chlorinating agent, first sampling, mg/L	4020	1340	16,900	2360
Chlorate in chlorinating agent, second sampling, mg/L	5400	1040	19,200	

NR: not reported

The information in Table 3 does not suggest any consistent explanation for the very high levels of chlorate seen in the three samples. While the chlorate content of the chlorinating agent used in Zone C was uniformly high across the two sampling periods, the chlorate concentration in the reticulation was only high at one of the sampling events. Similarly, the pH of the water in Zone B was low in both samples, but the reticulation chlorate concentration was only high for one sampling event. Chlorinating agent batch codes and/or expiry dates were provided for Zones A and B. In both cases the same batch of chlorinating agent was used in other supplies without obviously elevated chlorate concentrations in the reticulated supply.

It should not be assumed that the manufacturer's product is the cause of the elevated chlorate concentrations in the reticulation. The chlorate concentration in the chlorinating agent at Zone B was only a little over half the proposed SIL of 2000 mg/L.

### 3.3.2 DISTRIBUTION OF RETICULATION CHLORATE CONCENTRATIONS

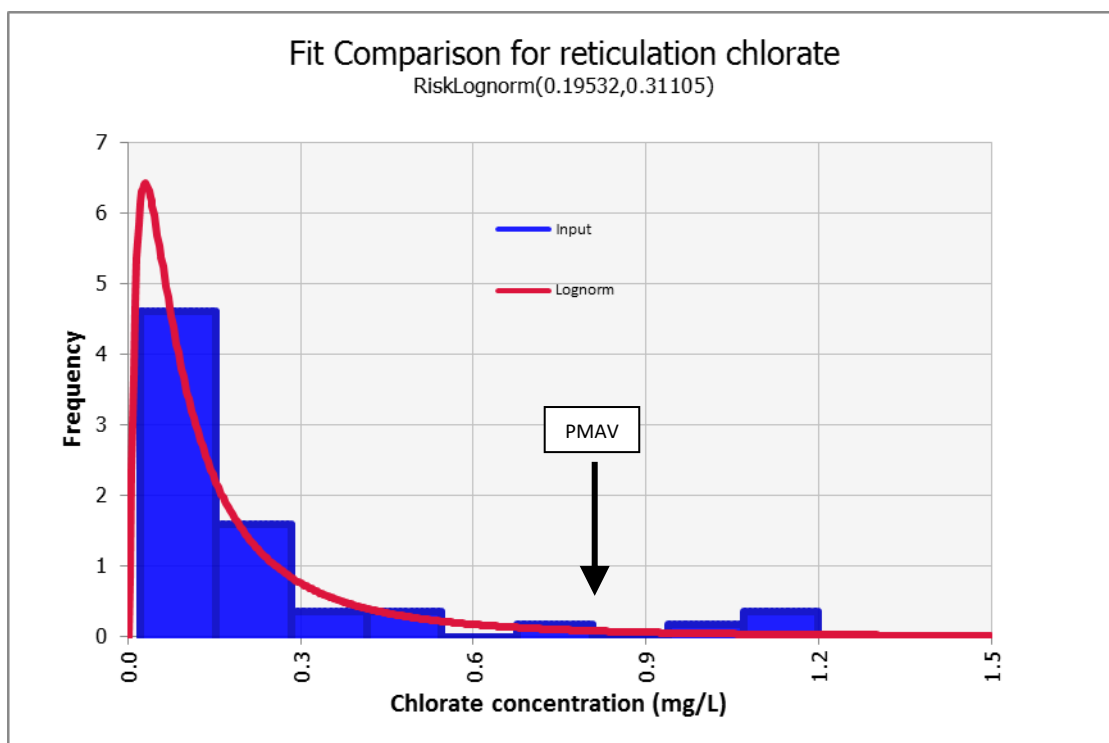
Contaminant concentrations in water and other environmental media are generally considered to conform to a right-skewed distribution, such as the lognormal. Figure 1 shows a histogram of the chlorate concentrations in reticulated water determined in the current survey, excluding the three very high concentrations. Figure 1 also shows the best-fitting lognormal distribution (@Risk software, Palisades Corporation) for these data.

As expected, the chlorate concentration results from the current survey conform approximately to a lognormal distribution. While there is a suggestion of a bimodal

distribution, with the bulk of samples containing a chlorate concentration of less than 0.6 mg/L and a smaller population of results at about 1 mg/L, the number of samples is too small to confirm that these two groups of results are really from separate populations.

Figure 1. Distribution of chlorate concentrations in reticulated New Zealand drinking-water (excluding very high concentrations)

### 3.3.3 ASSOCIATION OF RETICULATION CHLORATE CONCENTRATIONS WITH



### OTHER PHYSICOCHEMICAL DETERMINANDS

The relationship between the chlorate content of reticulated drinking-water and the pH, FAC or chlorinating agent chlorate content was examined using simple scatter plots. As the concentration of chlorate in chlorinating agents and in reticulation drinking-water is approximately lognormally distributed, these variables were log-transformed for scatter plot analysis. The relevant scatter plots, with the least-squares regression lines and  $R^2$  values are shown in Figure 2.

The results presented in Figure 2 are largely similar to an Italian study of swimming pool water, with insignificant associations found between pH and FAC and chlorate concentration (Righi et al., 2014).

While the directions of the associations shown in Figure 2 are consistent with expectation, the associations are uniformly weak. It is expected that the chlorate content of reticulated drinking-water would be positively associated with the level of chlorination and the chlorate content of the chlorinating solution. However, the  $R^2$  values for the scatter plots in Figure 2 suggest that the variables are only able to explain a small proportion of the observed variability of chlorate in drinking-water. The weak associations can be explained.

Disproportionation of the hypochlorite ion to produce chlorate only occurs at a significant rate at high hypochlorite concentrations. Any effect that pH has on the rate of this process will be evident in the chlorinating solution but not once the hypochlorite has been

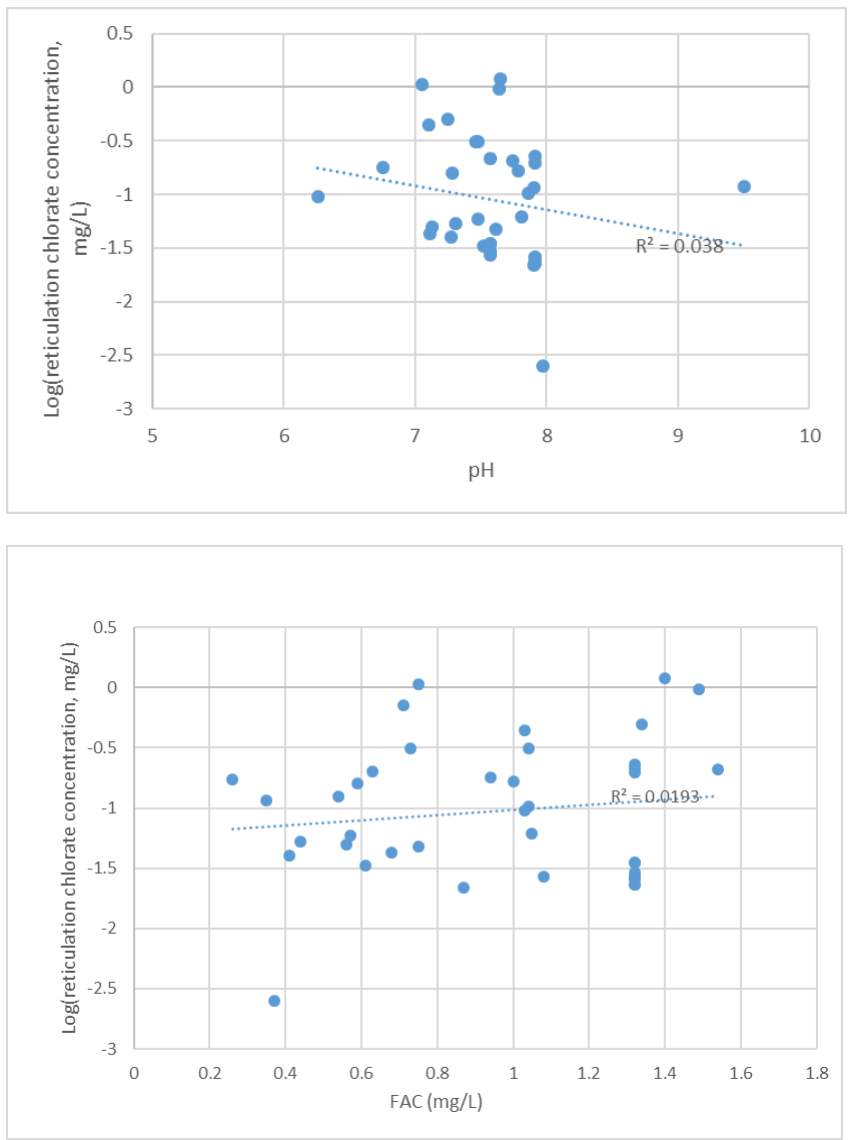


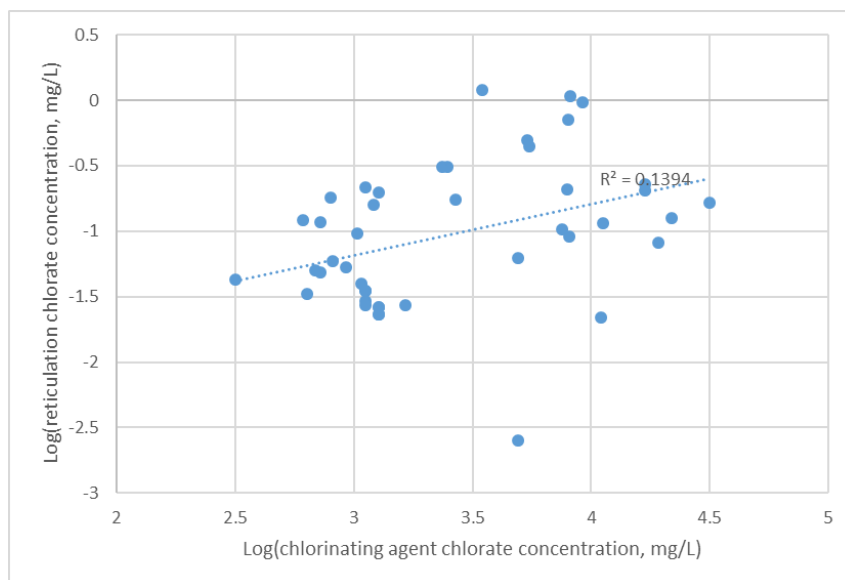
dosed into the bulk water flow and diluted. The dilution essentially quenches the reaction so that the pH in the reticulation does not have a significant effect on the chlorate concentration in the reticulation.

A factor leading to the variation in the relationship between the FAC concentration in the water leaving the plant and the chlorate in the reticulation is the variability in the ratio of hypochlorite concentration:chlorate concentration in the chlorinating solution. The extent of decomposition of the hypochlorite in the chlorinating solution is determined by factors such as the age of the solution, its metal content, temperature and the concentration of the hypochlorite itself. These factors are expected to vary between supplies and with time, as will the chlorine dose in use and therefore the chlorate concentration in the reticulation.

The chlorate concentration in the reticulation is expected to increase in proportion to the chlorate concentration in the chlorinating solution, assuming the dosing rate remains constant. However, the dosing rate is likely to vary with supply, and possibly within each supply, because the dose rate changes in response to changes in raw water quality.

Figure 2 Scatter plots of log reticulation chlorate concentrations against pH, FAC or log chlorinating agent chlorate concentration





### 3.4 CHLORATE CONCENTRATIONS IN CHLORINATING SOLUTIONS

#### 3.4.1 COMPARISON WITH SPECIFIC IMPURITY LIMITS

The data in Table 2 show that the chlorate concentrations in the chlorinating solutions ranged from 315 to 31,400 mg/L. The proposed SILs for chlorate in hypochlorite products are 2000 mg/L for chlorate in 13% sodium hypochlorite solution and 9000 mg/kg in 60% calcium hypochlorite solid.

None of the zones included in the survey used HTH for chlorination.

Thirteen of the 47 samples from chlorinating solutions were from plants identified as using brine electrolysis or products manufactured by brine electrolysis (as distinct from those using hypochlorite from the chlorine-caustic soda process). Of the 34 samples not using hypochlorite produced by brine electrolysis, the source of the hypochlorite was not identified for 10 samples. For the purposes of the statistics, the hypochlorite in these zones is assumed to be produced by a process other than electrolysis.

Of the 34 samples from zones in supplies not using hypochlorite produced by electrolysis, 23 (68%) contained chlorate at a concentration greater than 2000 mg/L. These samples were from 12 plants. None of the samples from zones in supplies using hypochlorite from electrolysis contained chlorate at a concentration greater than the proposed SIL. These zones receive water from three plants.

#### 3.4.2 RELATIONSHIP BETWEEN SIL EXCEEDANCE AND RETICULATION CHLORATE CONCENTRATIONS

The data in Table 4 are presented to examine the relationship between the chlorate concentration in the chlorinating solution and the chlorate concentration in the reticulated water. The data are discussed in section 4.

*Table 4 Relationship between the chlorate concentration in chlorinating solutions and the reticulation chlorate concentrations for both samplings<sup>1</sup>*

	<b>Number of zones (percentage of zones)</b>			
	First Sampling		Second Sampling	
		Reticulation		Reticulation

		chlorate concentration			chlorate concentration		
		Number of zones	Greater than 50% MAV	Greater than MAV	Number of zones	Greater than 50% MAV	Greater than MAV
<b>Chlorinating solution chlorate concentration</b>	Less than or equal to 2000 mg/L	9	0 (0%)	0 (0%)	7	1 (13%)	1 (13%)
	Greater than 2000 mg/L	12	4 (33%)	2 (17%)	11	3 (36%)	3 (27%)

<sup>1</sup> These data include results for all samples regardless of the hypochlorite source (eg, brine electrolysis), but include results for only two or the five Auckland zones for the reasons discussed in section 3.2.

## 4 DISCUSSION

### 4.1 INTRODUCTION

The study's results are not representative of chlorate concentrations in all drinking water supplies in New Zealand. The study's aim was to gather sufficient data to allow assessment of how the current concentrations of chlorate in hypochlorite products used in drinking water treatment influence chlorate concentrations in the reticulated water of supplies. To do this, the study focused on hypochlorite-treated supplies.

Although the sample size of the survey was relatively small, the study still provides valuable insights that will be helpful in setting the SILs for chlorate in hypochlorite products.

### 4.2 CHLORATE IN THE CHLORINATING SOLUTIONS

There is great variability in the chlorate concentrations in the chlorinating solutions, and also in the reticulation concentrations. Moreover, although there is evidence from the overall dataset that higher chlorate concentrations in chlorinating solutions lead to higher concentrations in the reticulated water, examination of data from individual supplies does not always show this. Multiple factors, in addition to the concentration in the chlorinating solution, influence the concentration of chlorate in the reticulated water. It was beyond the scope of this study to look at these in depth, but their interaction is likely to be contributing to the variability of the chlorate concentration in the reticulation. A more detailed study of individual supplies is required if a better understanding of the relationship is needed.

There is evidence from the study that hypochlorite produced by electrolysis (manufactured either on- or off-site) is more likely to contain chlorate at concentrations less than the SIL than other hypochlorite products used in this study<sup>2</sup>.

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<sup>2</sup> The authors are aware of a system that generates a chlorinating solution by spraying water onto solid HTH and mixing it with the bulk water immediately. This system is claimed to achieve low chlorate concentrations in the chlorinating solution. Such a system was not included in this survey.

Although a manufacturer of 13% sodium hypochlorite considered that chlorate concentrations in their product were likely to exceed the 2000 mg/L proposed SIL, the chlorate concentration in 32% of chlorinating solution (non-electrolysis) samples obtained in the survey was less than the SIL. This could result from: some manufacturing processes creating lower chlorate concentrations; differing periods of product storage (either before or after delivery to the water supplier) or dilution of the supplied product by the water supplier to reduce the rate of hypochlorite decomposition. The information collected with the survey does not allow the contributions from these possibilities to be assessed. However, chlorate concentrations measured by this manufacturer in their finished product varied from batch to batch (range: 1800–6300 mg/L). As the manufacturing process was the same for all batches, other factors appear to be causing the variability in this manufacturer's product.

Understanding how these factors influence chlorate concentration in the chlorinating solutions may allow a reduced likelihood of SIL exceedance in delivered products, and chlorate concentrations in reticulated waters to be managed to acceptable levels.

### **4.3 CHLORATE IN RETICULATED WATERS**

Chlorate was undetected (<0.005 mg/L) in only one of the 41 samples collected from reticulations (regarding the Auckland samples as being from a single zone), confirming that chlorate is present in the reticulated water of water supplies chlorinated with hypochlorite. In the survey, 22% of samples contained chlorate at a concentration of more than 50% of the pMAV, and in 15% of samples the chlorate concentration was greater than the pMAV. These percentages fall to 15% and 7%, respectively, if the three very high results are omitted from the calculation. Thus, if all data are retained in the calculation, a little over a fifth of supplies contained a chlorate concentration that could result in chlorate being assigned as a Priority 2 determinand to the zone and the consequent need for on-going monitoring.

The data in Table 4 show that zones receiving water chlorinated with a solution in which the chlorate concentration was less than the proposed 2000 mg/L SIL for chlorate are more likely to provide water of satisfactory quality (less than 50% of the pMAV) than those with a greater chlorate concentration in the chlorinating solution.

All reticulation samples from supplies using hypochlorite generated by brine electrolysis contained chlorate concentrations less than 50% of the pMAV. Note that the Auckland water supply zones receive water from the Waikato Water Treatment Plant where hypochlorite (generated by electrolysis) is used. However, water from this plant then passes through the Ardmore Water Treatment Plant where chlorination is by gas (with no chlorate input into the water). Passage through the second treatment plant effectively dilutes any chlorate in the water received from the Waikato Water Treatment Plant.

The survey collected two samples from each zone in all but three zones. While some zones show little difference in the reticulation chlorate concentrations in the two samples, in others the difference is quite marked. For this latter group, it is impossible to say which of the two results, if either, is typical of the zone. For zones with elevated chlorate concentrations, it is difficult to assess the public health risk associated with the presence of chlorate based on a single result. Although this risk cannot be quantified, the finding of at least one result with a chlorate concentration greater than 50% of the PMAV, is sufficient to show there is a risk that needs to be managed.

### **4.4 BROMATE AND PERCHLORATE**

Although not included in this study, perchlorate ion ( $\text{ClO}_4^-$ ) and bromate ion ( $\text{BrO}_3^-$ ) have also been shown to form in hypochlorite solutions.

Perchlorate does not presently have an MAV. However, should perchlorate be assigned an MAV, water suppliers using hypochlorite will need to undertake checks to assess how the typical concentration of this determinand in their water supply compares with the MAV. The steps noted in section 4.5 of this report for minimising chlorate formation also apply to perchlorate. Consideration will also need to be given to setting an SIL for perchlorate in the Guidance Note.

Bromate has a MAV (0.01 mg/L) and an SIL is assigned in the Guidance Note. The chlorate reduction steps outlined in section 4.5 also offer ways of minimising bromate formation. In addition to these, to limit bromate formation, high purity salt (low bromide) should be used when generating hypochlorite from brine electrolysis and low bromide water should be used for diluting chlorinating solutions. Chlorate and perchlorate, because of the vast excess of hypochlorite present, will continue to form, but bromate formation will eventually be limited by the amount of bromide present. As a guide, if all the bromide in a water is converted to bromate, a bromide concentration of approximately 0.006 mg/L will form bromate at the MAV.

#### **4.5 IMPLICATIONS FOR PRODUCT MANUFACTURERS AND WATER SUPPLIERS**

The study shows that chlorate concentrations in waters treated with hypochlorite can reach concentrations at which chlorate could be assigned as a Priority 2 determinand (50% of the MAV). This appears unlikely to be a problem for all water supplies treated with hypochlorite, because some processes used for generating hypochlorite result in lower chlorate concentrations in the chlorinating solution. Regardless, water suppliers using sources of hypochlorite with relatively low chlorate concentrations need to avoid practices, such as extended periods of storage of chlorinating solutions, that may result in elevated chlorate concentrations.

Actions both before and after delivery of a product to the water supplier can contribute to increases in chlorate concentration in the water received by the consumers. Consequently, both manufacturers and water suppliers need to be aware of how their actions may contribute to this problem. Both have a responsibility to take steps to reduce the likelihood of unacceptable chlorate concentrations reaching consumers. Stanford et al (2011) identified steps for minimising chlorate concentrations in chlorinating solutions. Manufacturers and water suppliers should be familiar with these steps and follow these recommendations wherever possible.

- a. Dilute stored hypochlorite solutions on delivery
- b. Store hypochlorite solutions at as low a temperature as practicably possible
- c. Maintain the pH of the stored hypochlorite solution in the range pH 11–13, after dilution
- d. Use hypochlorite solutions generated on-site (and calcium hypochlorite solutions) as soon as possible after preparation.
- e. Use filtered hypochlorite solutions (to remove metals) if purchasing hypochlorite solutions, or low-metal feed waters if generating the hypochlorite on-site (this also applies to the feed waters manufacturers use).
- f. Avoid extended storage times and use fresh hypochlorite solutions where possible.

Dilution of high concentration hypochlorite products as soon as practicable will be the most efficient step in reducing chlorate concentrations in reticulated water. Consequently, discussions between manufacturers and water suppliers over the

possibility of the manufacturer offering lower concentration hypochlorite product (so that hypochlorite is stored at a lower concentration before delivery) may prove valuable.

There are two other points that are specifically the water supplier's responsibility when managing chemical risks associated with the use of hypochlorite solutions.

- a. Regular monitoring of chlorate in the reticulated water should be undertaken as part of the water safety plan of a supply using hypochlorite. There should also be checks on the bromate concentration (not included in this survey) in the reticulated water under two circumstances:
  - i. the hypochlorite is generated from brine
  - ii. purchased hypochlorite product (manufactured by any process) is diluted (because of the possibility of bromide in the dilution water).
- b. As with managing the public health risk from other disinfection by-products, water suppliers must avoid compromising disinfection when attempting to minimise chlorate and/or bromate formation.

#### **4.6 CONSIDERATIONS FOR THE GOOD PRACTICE NOTE**

The finding of elevated chlorate concentrations in some water supplies included in this survey has led the authors to re-examine some aspects of the Guidance Note.

- a. Reporting chlorate concentrations in the delivered product

Water suppliers can be helped in their management of the risk arising from chlorate by knowing the concentration of chlorate in the delivered solutions they receive. The Guidance Note presently requires manufacturers to provide the water supplier with a certificate

"... that states that the material furnished in accordance with the purchaser's order complies with all applicable requirements of this Guide. This is to include the concentrations of properties listed in section 2.3 and 2.2 using tests undertaken at frequencies outlined in section 3.4."

Section 3.4 of the document requires an "annual" testing frequency for chlorate if it exceeds 50% of its SIL.

Given the range of factors that can influence the rate of chlorate formation, the helpfulness of an annual check on managing chlorate concentrations in a product is questionable. This concern is supported by the manufacturer's data noted in section 4.2, which showed a substantial variation in the range of chlorate concentrations measured in their finished product over time.

**For these reasons, the appropriateness of the annual testing frequency for chlorate should be re-examined, or manufacturers need to demonstrate that the control they have over the chlorate concentration in their finished product is sufficient to assure water suppliers that a once-yearly test is representative of each product batch they receive.**

- b. Basis of the SIL calculation

The proposed SIL calculation assumes that the chlorine dose is 5 mg/L. For most water supplies this is expected to be an over estimation of the dose used. A reduction of the

assumed dose for the calculation would result in a higher SIL, which could be more easily met by manufacturers, and so reduce the concern about the currently proposed SIL.

However, this step would not help in reducing the chlorate concentrations in the water provided to consumers. The study has shown that chlorate concentrations exceeding the SIL in the chlorinating solution can lead to chlorate concentrations in the reticulated water exceeding the MAV as well as 50% of the MAV. **The survey's findings do not support raising the proposed SIL.**

## 5 CONCLUSIONS

New Zealand drinking-water supplies disinfected with sodium or calcium hypochlorite were identified and sampled for chlorate, pH and FAC analysis on one or two occasions. The chlorate concentration was also determined in the chlorinating solution used at the water treatment plant. Chlorate was detected within the reticulation system of all hypochlorite-treated supplies included in the current study (n = 25), at least once. Three supplies were identified with particularly high chlorate concentrations (6.5, 42.9 and 92.1 mg/L) in their reticulated water on one occasion, but there is uncertainty over the validity of these results. These three supplies did not have remarkable chlorate concentrations on the other sampling occasion (0.10, 0.50 and 0.08 mg/L, respectively) and the physicochemical characteristics of the water did not suggest a reason for the high chlorate concentrations.

The remaining measured chlorate concentrations were in the range <0.005–1.2 mg/L (mean 0.24 mg/L), which was consistent with the results of overseas surveys of chlorate in drinking-water. There were only weak and non-significant correlations between the chlorate concentration in the reticulated water and the FAC and pH of the water leaving the plant or the chlorate concentration in the chlorinating solution.

Several conclusions are drawn from the study.

- Potentially health-significant chlorate concentrations do arise in New Zealand's reticulated waters as the result of the use of hypochlorite. Some are in excess of the MAV.
- Chlorate concentrations in reticulated water and chlorinating solutions are variable. Chlorinating solutions containing chlorate concentrations less than the proposed SIL are less likely to be associated with chlorate concentrations exceeding 50% of the MAV in the reticulation.
- There is evidence that chlorinating solutions prepared by electrolysis, online and as a batch product at low hypochlorite concentration, are less likely to contain chlorate at concentrations exceeding the proposed SIL, and that the SIL is achievable, although this is more difficult for higher strength hypochlorite products.
- Because of the factors leading to elevated chlorate concentrations in chlorinating solutions, manufacturers and water suppliers share responsibility for taking steps to manage the risk associated with chlorate in water supplies.
- Several steps have been identified for reducing the chlorate concentration in chlorinating solutions. The most important is dilution of the hypochlorite solution strength.

- There are implications for the Guidance Note. The frequency at which manufacturers are required to test chlorate in their product needs to be re-examined, and the survey's findings do not support raising the proposed SIL.
- Several factors can contribute to the presence of elevated chlorate (and other oxyhalides) concentrations in drinking water chlorinated using hypochlorite. Water suppliers using hypochlorite need to be aware of these factors and ensure that this risk is managed in their water safety plans. This should include adequate monitoring as a check that their preventive measures are effective.

The study's aim was not to obtain a detailed understanding of the factors influencing the chlorate concentration in the reticulated water. A new study with different aims would be required for this purpose and, given the information already available on steps for reducing chlorate concentrations, the value of a generic study would need to be carefully considered. Greater value for individual suppliers might be obtained from investigations of their specific supplies.

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