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International Journal of
Dairy Technology
SDT Society of Dairy Technology
doi: 10.1111/1471-0307.13012

RESEARCH ARTICLE

# Chlorinated water as a source of chlorate contamination in farm bulk milk

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*The potential for chlorinated water to cause chlorate contamination of milk was evaluated at both laboratory and field level. It was found that for such contamination to occur, direct contact of water and milk was necessary. To minimise the opportunity for chlorinated water to cause chlorate contamination of milk, it is vital to ensure that milk handling equipment is engineered to provide for proper drainage of water and that all necessary steps are taken to prevent the adulteration of milk with water.*

**Keywords** Chlorine, Chlorate, Milk, Residue, Water.

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## INTRODUCTION

Chlorate is derived from the degradation of chlorine, particularly the degradation of sodium hypochlorite and chlorine dioxide (Gordon *et al.* 1997; Stanford *et al.* 2011; Kriem 2017; McCarthy *et al.* 2018). Chlorate is a goitrogen and therefore, poses a risk to the function of the thyroid gland, particularly in infants and young children (McCarthy *et al.* 2018). Due to the aforementioned health risks, chlorate is a statutorily regulated residue in the EU, with a limit of 0.10 mg/kg applicable for milk in its ready-to-use state (Commission EU 2020). Chlorate residue has previously been detected in farm bulk milk sampled in Italy (Nobile *et al.* 2022) and in the Republic of Ireland (ROI) (Paludetti *et al.* 2019). Chlorate is considered a critical parameter by the Irish dairy industry due to the fact that approximately, 13% of the world's infant milk formula is produced in the ROI (Bord Bia 2020). The Irish dairy industry's primary response to the issue of chlorate residue has been to mitigate against it as a contaminant of both the manufacturing milk pool and finished dairy products/ingredients *via* prohibiting the use of chlorine-based detergents and sanitisers on farms and in processing plants in the ROI. This 'chlorine-free' resolution came into effect on 1st January 2021 (Phelan 2019). Notwithstanding this, direct chlorine use *via* cleaning in place is not the only source of chlorate within the dairy production chain. Water, particularly that which has been treated using chlorination methods that are conducive to chlorate formation, for example, chlorine dioxide or sodium hypochlorite is another potential source of chlorate (Alfredo *et al.* 2015; Kriem 2017; McCarthy *et al.* 2018; Gleeson *et al.* 2022). Internationally, chlorine is a very common method of disinfecting water (Kettlitz *et al.* 2016). Water sampled in the United Kingdom, Spain, France, and Belgium contained mean chlorate levels of 0.07, 0.148, 0.184, and 0.378 mg/L, respectively (Kettlitz *et al.* 2016). Mean chlorate levels in Canadian water supplies were 0.22 mg/L in summer and 0.13 mg/L in winter (Kettlitz *et al.* 2016). The higher chlorate levels in summer can be attributed to higher rates of chlorination in the summer months when warmer weather is likely to increase the microbial load of water (Kettlitz *et al.* 2016). Asami *et al.* (2013) reported chlorate levels ranging from 0.034–0.14 mg/L in water sampled in Japan. A limited number of water samples ($n$ = 10) taken in the ROI displayed chlorate levels which ranged from 0.105–0.396 mg/L (Twomey *et al.* 2023). Statutory limits for chlorate levels in water vary in different jurisdictions and regulatory bodies. For example, the

European Union imposes maximum residue limits of 0.70 mg/L for chlorate in chlorinated water and 0.25 mg/L where chlorine has not been added (Council EU 2020). Alternatively, Canadian authorities impose a maximum allowed concentration of 1 mg/L (Kettlitz *et al*. 2016).

Notwithstanding the availability of international data regarding chlorate levels in water, little is known about the levels and dynamics of chlorate in water, representative of that found in chlorinated water supplies in the ROI. Moreover, there is a paucity of knowledge regarding the subsequent contamination potential that chlorate in water has on milk. Anecdotally, it is thought that when used as part of the milking equipment cleaning process, water that contains chlorine and by association, chlorate could result in chlorate residues in bulk tank milk. Of 95 dairy farms in the ROI which were surveyed during 2022, one-third were found to source their water from either public or group water supplies (Gleeson and Twomey, unpublished), which commonly treat water with chlorine (National Federation of Group Water Schemes 2017; Irish Water 2021). Hence, the prevalence of farms utilising chlorinated water is notable. Moreover, chlorate was detected in bulk tank milk in a number of farms that used chlorine-free cleaning products and this suggests that it may be the result of chlorinated water use (Gleeson *et al*. 2022). Therefore, chlorinated water is a credible concern for the dairy industry with regard to milk quality from a chlorate perspective, leading to the overall objective of this study being to establish if chlorinated water can cause chlorate contamination of milk. To achieve this objective, both laboratory and field-based investigations were conducted to establish: (1) if chlorate levels in water increase linearly with increasing total chlorine levels in water; (2) if ageing sodium hypochlorite can cause elevated chlorate levels in water; and (3) if waters (containing chlorate) can cause chlorate occurrence in milk.

## MATERIALS AND METHODS

### Laboratory experiment: The influence of total chlorine level and sodium hypochlorite age on chlorate levels in water

Treatments ($n = 6$) consisted of a non-chlorinated control plus five chlorinated waters containing 0.50, 1.00, 1.50, 2.00 and 2.50 mg/L of total chlorine (free plus sequestered chlorine), respectively. These treatments were based on the levels of total chlorine found in public and group water supplies in ROI (National Federation of Group Water Schemes 2017; Irish Water 2021). The treatments were created in the laboratory using well water and a 100 mg/L 10% sodium hypochlorite stock solution. Well water (untreated) was sourced from a deep well on a commercial dairy farm and inherently contained 0.0028 mg/L of chlorate. This is likely attributed to atmospheric chlorate formation (Rao *et al*. 2010). In advance of chlorination, the well water was analysed for total bacteria count (TBC). The 100 mg/L stock solution was created by adding 1 g (0.85 mL) of sodium hypochlorite (Micro-Bio, Cork, Ireland) to 1 L of well water followed by thorough inversion. The sodium hypochlorite was stored in a bunded chemical store room, as per the manufacturer's instructions, that is, in an opaque container, out of direct sunlight and heat and segregated from all acidic chemicals. The amount of stock solution required to make each treatment depended on the target total chlorine level. Once that was determined, the required volume was added to individual 500 mL subsamples of water using a 5 mL serological pipette (OCON Chemicals, Cork, Ireland) followed by thorough inversion. Following this, 12 mL of water was taken from each treatment and a confirmatory test for total chlorine content was conducted using an eXact® Micro 20 chlorine meter (Campion Pumps, Co., Tipperary, Ireland). This test was carried out *in situ* and repeated three times. Following confirmation of total chlorine levels, each treatment was sampled in triplicate (3 × 40 mL samples) by pouring water into 50 mL polypropylene tubes (Sarstedt Limited, Wexford, Ireland). These water samples were then frozen at −20°C. An additional 20 mL water sample was also retained from each treatment and frozen at −20°C. This sample was retained for use in the subsequent milk spiking experiment.

The experiment was repeated at four individual time points over a 6-month period in order to account for any impacts that ageing of sodium hypochlorite had on chlorate levels in water. The experiment was conducted when the sodium hypochlorite had just been produced (0 days old) and repeated when it was 62, 119 and 175 days old; hereafter these time points are referred to as D 0, D 62, D 119 and D 175. The same methodology (as described above) was followed at each of the four time points. In total, over the 6-month period, 12 samples were yielded from each treatment resulting in 72 samples overall.

### Laboratory experiment: Chlorate transfer from water to milk

Water samples which were retained in a frozen state (−20°C) from each of the six water treatments created over the aforementioned 6-month period were defrosted in a refrigerated cold room (≤6°C) overnight (20 h). A pilot study to investigate the effect; if any, that freezing and subsequent defrosting had on chlorate levels in waters was conducted in advance of the spiking experiment and these processes were not found to have any significant impact on chlorate levels in water (results not shown). Each water treatment had four water samples which were used for spiking, one sample from each of D 0, D 62, D 119 and D 175 ($n = 24$ in total).

A single, 4 L batch of raw milk was taken from the bulk tank on the dairy research farm at Teagasc, Moorepark, Fermoy, Co. Cork, Ireland using a single 5 L glass bottle


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(DWK Life Sciences GmbH, Mainz, Germany). The bulk tank was thoroughly agitated before the milk was obtained *via* the bottom outlet of the tank, but not before the first 3–5 L of milk was run to waste. The milk was stored in a refrigerated cold room (≤6°C) until required (approx. 3 h storage). In advance of spiking, this milk was sampled in triplicate for the purposes of TBC and chlorate analysis. These samples were 20 mL in volume and taken in 30 mL Sterilin™ tubes (Sparks Lab Supplies Limited, Dublin, Ireland). Following this, 24 × 100 mL aliquots were taken from the 4 L batch of milk using a 100 mL graduated cylinder (Fisher Scientific Ireland Ltd., Dublin, Ireland). Each 100 mL aliquot was then transferred into a 250 mL bottle (DWK Life Sciences GmbH), capped and stored in a refrigerated cold room (≤6°C) until spiked (stored for 1.5 h maximum). Both the original batch and the 100 mL aliquots of milk were regularly inverted to maximise the homogeneity of the milk, pre and post-spiking.

A spiking rate of 2% was determined to be sufficient to yield a display of chlorate (if present) in milk *via* a series of pilot trials (results not shown). A 1000 μL pipette was used to transfer 2 mL of water (2%) to each 100 mL aliquot of milk. A new pipette tip (Sarstedt Limited) was used for each spike to prevent cross-contamination. Post-spiking, each spiked milk sample was thoroughly inverted and subdivided in triplicate, *via* pouring 25 mL of spiked milk into 3 × 50 mL polypropylene tubes (Sarstedt Limited). Each sample was then frozen at −20°C. The bulk milk used for the spiking experiment contained detectable levels of chlorate (0.0025 mg/kg). Therefore, all results presented for this element of the experiment are net chlorate results. Net chlorate results were calculated by subtracting the inherent level of chlorate in the bulk milk from the laboratory result to determine the actual level of chlorate present as a result of spiking.

### Field experiment: Rinsing a milking plant with chlorinated water

A field experiment was conducted to evaluate the effects of using chlorinated water in a milk production environment. This involved rinsing a milking machine with water containing different levels of total chlorine. This experiment was carried out on the 30 unit side by side milking parlour (Dairymaster, Co. Kerry, Ireland) at the dairy research farm at Teagasc Moorepark, Fermoy, Co. Cork, Ireland. It was completed across a 4-week period in November/December 2021 and conducted at afternoon milkings only. The design and operation of the milk transfer equipment was the same as that described in O'Connell *et al*. (2016), with the exception of the cluster flushing system which was switched off during the experiment. The bulk tank was not included in this experiment due to logistical limitations. At each milking, cows' teats were disinfected using a chlorohexidine-based teat disinfectant (Deosan Teatfoam Advance AG104; Diversey Hygiene, Dublin, Ireland) and wiped with single-use paper towels in advance of cluster attachment. The milking machine wash routine consisted of a post-milking rinse with cold water at a rate of 12 L per milking unit followed by a hot wash (75–80°C; 9 L/unit) with chlorine-free caustic detergent on 11 occasions per week (Liquid Gold *CF*; Dairymaster) and phosphoric acid (Aval Platinum Descaler; Carbon Group, Co. Cork, Ireland) on three occasions per week. After each hot wash the plant was rinsed with cold water at a rate of 12 L per milking unit. Approximately, 2 h before each milking a 0.1% peracetic acid sanitising solution (Aval ThermoKlense 5% Peracetic Acid; Carbon Group) was flushed through the plant at a rate of 12 L per unit.

Three treatments were applied as rinses using chlorinated water containing 0.10, 0.50 and 2.00 mg/L of total chlorine, respectively. Each treatment was applied three times and in a random order. The total chlorine level of the three treatments were based on the minimum (0.10 mg/L), average (0.50 mg/L) and maximum levels (2.00 mg/L) found in chlorinated water supplies in the ROI (National Federation of Group Water Schemes 2017; Irish Water 2021). The water used on the Moorepark farm was chlorinated at source to a target total chlorine level of 0.10 mg/L. Therefore, it was not possible to use non-chlorinated water as a control treatment as all water used during this experiment contained a level of total chlorine. In place of a chlorine-free rinse, the 0.10 mg/L may be interpreted as the control.

The application of these three chlorinated treatments involved the creation of a 500 mg/L sodium hypochlorite stock solution by adding 5 g (4.25 mL) of 10% sodium hypochlorite (Micro-Bio) to 5 L of deionised water using a 1000 μL pipette, followed by thorough inversion. The sodium hypochlorite used was from the same batch that was being used to treat the water supply at source. The required amount of the stock solution was then added to the water in the rinse trough (356 L). The amount required was based on the exact amount of total chlorine present in the tap water. For example, to create rinse water with 0.50 mg/L where the tap water already contained 0.10 mg/L sufficient stock solution to contribute 0.40 mg/L was required. This was calculated as follows:

- 0.40 × 356 000 mL = 142 400 mg of chlorine required
- 142 400 mg ÷ 500 mg/L = 285 mL of standard solution required

The chlorinated rinsing treatments were created and applied in the 2-h period preceding afternoon milking (3 pm). The standard chlorine-free wash routine had completed in its entirety in advance of each rinse treatment being applied. Before each chlorinated water rinse was flushed through the milking plant, three samples were obtained from the trough using a single 180 mL plastic



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dipper (International Scientific Supplies Ltd., West Yorkshire, UK). Each sample was then transferred to a 50 mL polypropylene tube (Sarstedt Limited). A new 180 mL dipper was used at each rinsing event. Rinsing took seven and a half minutes to complete, plus another 2 min for the plant to drain and purge. During rinsing, three samples of water were taken *via* an in-line sampling tap (located on the transfer line entering the milk filter). One sample was taken 4 min post-start, a second was taken at 6 min post-start and the third sample was taken at the end of the drainage/purge cycle. Water samples taken from both the trough and the in-line tap were tested for total chlorine (*in situ*) and retained for chlorate analysis. Water was sampled both pre- and post-rinsing to ascertain how much chlorate, if any, leached onto milk contact surfaces.

Afternoon milking immediately succeeded each rinsing treatment. Milk samples were obtained from row 1 ($n = 30$ cows), row 2 ($n = 30$ cows) and row 3 ($n = 30$ cows) at each of these milkings, *via* the in-line sampling tap (same as that used to sample the rinse water). The milking procedure was observed to ensure that clusters were attached to all cows in each respective row before any milk sampling was conducted. This was done to ensure that the milk sampled was as representative of each row of cows as possible. Samples (300 mL) were taken using clean glass bottles (DWK Life Sciences GmbH). Following thorough inversion of the 300 mL sample, it was aliquoted into 6 × 25 mL sub-samples. Three of these samples were designated for chlorate analysis and three were retained for freezing point depression (FPD) analysis/as spare samples. Surplus milk was discarded. Both water and milk samples were kept on ice until frozen at −20°C.

### Chlorine analysis

Total chlorine levels were determined using the eXact® Micro 20. This is a N, N-diethyl-p-phenylenediamine (DPD) test system that is accepted by the United States Environmental Protection Agency (USEPA) (DIN Standard 38 408 G4, ISO 7393/2) for the analysis of total chlorine which is measured in parts per million (ppm) (Industrial Test Systems Incorporated 2019).

### Chlorate analysis

Chlorate analysis was conducted at the Teagasc Food Research Centre in Ashtown, Dublin 15, Ireland using ultra-performance liquid chromatography coupled with tandem mass spectrometry (UPLC–MS/MS) (Moloney *et al*. 2021). The reporting limits for these analyses were 0.00020 mg/L and 0.0020 mg/kg for water and milk, respectively.

### Total bacteria analysis

Total bacteria counts of both water and milk used during the laboratory experiment were conducted in the Milk Quality Laboratory, Moorepark, Fermoy, Co. Cork, Ireland. using 3M Petrifilm aerobic count (AC) plates (Technopath, Tipperary, Ireland). The total number of colonies on each AC plate was quantified using a 3 M Petrifilm reader (Technopath). The tests were conducted as per standard methods for the evaluation of dairy products (Laird *et al*. 2004).

### Milk freezing point analysis

The analysis of freezing points in fresh and defrosted milk samples from both the laboratory and field experiments was conducted at the Teagasc Milk Quality Laboratory using a Milkoscan 7. Values of <0.500°C indicated the presence of extraneous water. A pilot trial was conducted to see if significant differences existed between freezing point values in fresh and frozen milks. No significant differences were observed (results not shown).

### Statistical analysis

Results were analysed using the Tukey, Hovtest and Welch tests as part of the general linear model (GLM) procedure in SAS version 9.4 (SAS Institute Inc., Cary, NC, USA, 2016) with the significance level set at $\alpha = 0.05$.

## RESULTS

### Laboratory experiments

The levels of chlorate detected in waters with increasing levels of total chlorine increased in a linear fashion (Figure 1), but not all treatments were significantly different. Relative to the chlorate levels detected in the control water treatment, chlorate levels from the 1.00, 1.50, 2.00 and 2.50 mg/L treatments were significantly higher ($P < 0.05$). Insignificant differences were apparent between all adjacent treatments ($P > 0.05$). For example, the 1.00 mg/L treatment displayed chlorate levels that were not significantly different from those detected in both the 0.50 and 1.50 mg/L treatments (Table 1).

Water chlorinated at D 0 of the experiment had significantly lower chlorate levels than waters created at D 64, D 119 and D 175 ($P < 0.05$), but no significant differences were found between chlorate levels in waters created at D 64, D 119 and D 175 ($P > 0.05$) (Table 2). The TBC's of the well water used at D 0, D 64, D 119 and D 175 were $\log_{10}$ 3.23, 0.70, 2.02 and 0 cfu/mL, respectively.

Chlorate was detected in milk spiked with water from all treatments, except the control treatment. The only chlorate detected in the control treatment was that inherently present in the milk (0.0025 mg/kg). All chlorate levels being considered here are those present as a direct consequence of spiking, that is, levels present after the inherent 0.0025 mg/kg was subtracted. Chlorate levels detected in spiked milks were not significantly different from each other ($P > 0.05$) (Table 3). The milk used for the spiking experiment had a TBC of $\log_{10}$ 3.59 cfu/mL.

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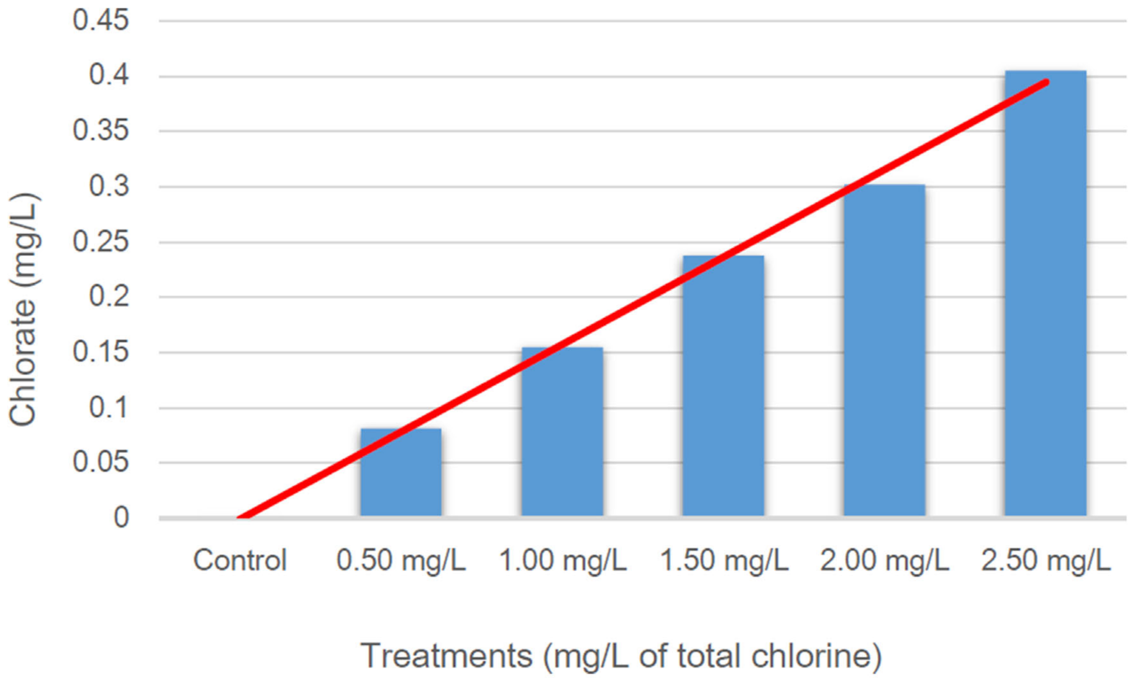


**Figure 1** The trend displayed by chlorate levels in water with increasing levels of total chlorine. This data corresponds to the values presented in Table 1. The control treatment contains no added chlorine.

**Table 1** Chlorate levels in waters containing increasing levels of total chlorine.

| Treatment[1] | No. samples[2] | Mean chlorate (mg/L)[3] | SD (mg/L) |
|---|---|---|---|
| Control | 12 | 0.0003[a] | 0.001 |
| 0.50 mg/L | 12 | 0.0813[ab] | 0.035 |
| 1.00 mg/L | 12 | 0.1547[bc] | 0.065 |
| 1.50 mg/L | 12 | 0.2377[cd] | 0.108 |
| 2.00 mg/L | 12 | 0.3019[de] | 0.137 |
| 2.50 mg/L | 12 | 0.4048[ef] | 0.178 |

[1]Treatment refers to the total chlorine level in water samples.
[2]No. samples refers to the total number of samples created and analysed.
[3]Chlorate levels presented are the means of all samples in each treatment; values with different superscripts are significantly different ($P < 0.05$); the control treatment was non-chlorinated well water.

### Field experiment

Rinse water which contained greater total chlorine levels also contained greater chlorate levels (Table 4). Regarding the 0.10 and 0.50 mg/L treatments, significant differences were not found between chlorate levels in rinse water before and after it was used to rinse the milking plant ($P > 0.05$). However, chlorate levels in the rinse water that contained 2.00 mg/L were significantly lower when compared before and after rinsing ($P < 0.01$) (Table 4). Chlorate was detected in milk sampled from the first row of cows milked at each milking but not from the second and third rows, regardless of treatment. Extraneous water was detected in milk sampled from the first row of cows milked but not from the second (FPD analysis was not conducted on milk from the third row). Chlorate levels in milk from each rinse treatment were shown to be similar ($P > 0.05$), as were FPD results (Table 5). Based on routine milk quality analysis conducted by the milk purchaser, the average TBC for the milk produced on the Moorepark dairy farm over the November/December period of 2021 was $\log_{10}$ 4.41 cfu/mL.

## DISCUSSION

In accordance with previous research (Stanford *et al*. 2011), this study showed that higher chlorate levels in water were associated with higher total chlorine levels in water; the total chlorine levels in question in this study are representative of those found in Irish supplies. This suggests that water networks that are chlorinated at higher rates of total chlorine are likely to have higher levels of chlorate present in water supplies. These higher rates of chlorination may occur at the initial treatment stage only or result from a combination of initial chlorination and secondary/booster dosing of additional chlorine along water pipelines (Environmental Protection Agency 2011).

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**Table 2** Chlorate levels in waters chlorinated using sodium hypochlorite of increasing age.

| Day[1] | No. samples[2] | Mean Chlorate (mg/L)[3] | SD (mg/L) |
|---|---|---|---|
| 0 | 18 | 0.065[a] | 0.043 |
| 62 | 18 | 0.199[b] | 0.149 |
| 119 | 18 | 0.265[b] | 0.186 |
| 175 | 18 | 0.260[b] | 0.184 |

[1]Day refers to sodium hypochlorite used for chlorination at 0, 62, 119 and 175 days post-manufacture, respectively.
[2]No. samples refers to the total number of samples created and analysed.
[3]Chlorate levels presented are the means of all samples in each treatment; values with different superscripts are significantly different ($P < 0.05$).

**Table 3** Chlorate levels in milks spiked with chlorinated waters containing increasing levels of total chlorine.

| Treatment[1] | No. samples[2] | Mean chlorate (mg/kg)[3] | SD (mg/L) |
|---|---|---|---|
| Control | 4 (0) | Not detected | Not detected |
| 0.50 mg/L | 4 (2) | 0.0025[a] | 0.0007 |
| 1.00 mg/L | 4 (3) | 0.0043[a] | 0.0012 |
| 1.50 mg/L | 4 (3) | 0.0060[a] | 0.0010 |
| 2.00 mg/L | 3 (2) | 0.0095[a] | 0.0007 |
| 2.50 mg/L | 4 (4) | 0.0085[a] | 0.0044 |

[1]Treatment refers to the total chlorine level in water samples.
[2]No. samples refers to the total number of samples created and analysed.
[3]Chlorate levels presented are the means of all samples in which chlorate was detected (>0.0020 mg/kg); the number of samples in each treatment in which chlorate was detected as a consequence of spiking are presented in parentheses in the table; values with different superscripts are significantly different ($P < 0.05$). Milk spiked with water from the control treatment is noted as having no chlorate detected because chlorate was not detected in these milks as a consequence of spiking, the only chlorate detected in them was that inherently present in the milk (0.0025 mg/kg), which was not included in the final chlorate levels of any treatment.

**Table 4** Chlorate levels in chlorinated rinse water pre- and post-rinsing of the milking plant.

| | Pre-rinsing ($n$ = 27) | Post-rinsing ($n$ = 27) | |
|---|---|---|---|
| Treatment[1] | Mean chlorate (SD) (mg\L)[2] | Mean chlorate (SD) (mg\L)[2] | $P$-value |
| 0.10 mg/L | 0.079 (0.0029) | 0.081 (0.0058) | >0.05 |
| 0.50 mg/L | 0.112 (0.0055) | 0.111 (0.0083) | >0.05 |
| 2.00 mg/L | 0.325 (0.0133) | 0.290 (0.0125) | <0.01 |

[1]Treatment refers to the total chlorine level in water samples.
[2]Chlorate levels presented are the means of all samples in which chlorate was detected (>0.00020 mg/L); results are presented within each row. A total of 27 samples were analysed both pre- and post-rinsing, respectively; 9 from each treatment.

**Table 5** Chlorate and freezing point depression levels of in-line milk samples taken from row one.

| Treatment[1] | No. samples[2] | Mean chlorate (SD) (mg/kg)[3] | Mean FPD (SD) (°C)[4] |
|---|---|---|---|
| 0.10 mg/L | 9 | 0.017 (0.010) | 0.436 (0.050) |
| 0.50 mg/L | 9 | 0.024 (0.018) | 0.431 (0.081) |
| 2.00 mg/L | 9 | 0.020 (0.004) | 0.497 (0.009) |
| $P$-value | | >0.05 | >0.05 |

[1]Treatment refers to the total chlorine level in water samples.
[2]No. samples refers to the total number of samples created and analysed.
[3]Chlorate levels presented are the means of all samples in which chlorate was detected (>0.0020 mg/kg) (all samples).
[4]FPD levels are the means of the FPD results from all samples in each treatment; results are presented within each column.

Based on the fact that chlorate levels in sodium hypochlorite products increase with age (Gleeson 2016), it was expected that using aged sodium hypochlorite would result in significantly higher levels of chlorate in water. Chlorate levels present in water after using D 0 sodium hypochlorite were significantly lower ($P < 0.05$) than those detected from D 62, D 119 and D 175, respectively. However, in contrast to expectation, chlorate levels in water chlorinated with sodium hypochlorite from D 62, D 119 and D 175 were similar. This finding does not dispute the fact that the ageing of chlorination agents can lead to increased chlorate development as presented by Gleeson (2016), because from a practical perspective, its use did result in higher levels of chlorate in water. These statistically insignificant increases in chlorate in water may be attributed to the combined benefits of proper storage and moderate ionic strength (as observed in the current study) where sodium hypochlorite is concerned (Stanford *et al*. 2011; Breytus *et al*. 2017).

From a statistical perspective, chlorate levels in water were not found to have a significant impact on chlorate levels in milk during the laboratory spiking experiment. However, when viewed from a practical perspective, when water containing increasing levels of total chlorine and by association, increasing levels of chlorate was used to spike milk, increasing chlorate levels in milk were observed from a numerical perspective. The practical significance of this outcome is important due to the critical requirements of dairy processors with regard to meeting both legislative obligations and customer expectations.

The effect that the addition of chlorinated water may have on chlorate levels in milk may be observed at a larger scale in the field experiment. The combination of chlorinated

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water and milk from the first row of cows resulted in increased chlorate in that milk (based on the assumption that milk directly harvested from the mammary gland does not contain chlorate). The combination of rinse water containing chlorate with milk was evidenced by the depression in freezing point.

While the presence of extraneous water was the most likely cause of increased chlorate in the milk from the first row of cows, some chlorate may have leached onto milk contact surfaces as well.

Notwithstanding the aforementioned leaching of chlorate from water, within the confines of this study, it can be concluded that leaching of chlorate onto milk contact surfaces is not a significant source of contamination. This is supported by the levels of extraneous water detected in milk which contained detectable levels of chlorate. Moreover, the treatment with the lowest FPD value (which is indicative of higher levels of extraneous water) was also the treatment with the highest level of chlorate in milk.

Based on these outcomes, it is evident that chlorate contamination of milk is influenced by farm management practices, particularly drainage of milk handling equipment, that is, the milking plant and bulk milk tank (Irish Milk Quality Co-operative Society 2009). Ample drainage can be provided by utilising drainage points throughout the milking system, particularly those on the receiver vessel and milk filter housing. Milking clusters and long milk tubes should also be monitored for water retention and remedial action taken as required. Examples of such action are the installation of drainage points on wash jetters and removal of clusters from jetters in advance of vacuum being applied to allow any water in the long milk tube to drain away. Under vacuum, this water may be drawn into the milk line and ultimately into the bulk milk tank. The bulk milk tank itself should be inspected regularly to ensure that water is not being unnecessarily retained in the tank post-washing. Furthermore, the expulsion of milk from the system at the end of milking should ideally be done using air as opposed to water (Ryan and Donworth 2016). This is especially pertinent where chlorinated water is employed as it may inadvertently lead to chlorate entering the bulk milk tank.

Results from the laboratory experiments suggest that the impact that using water containing chlorate on the overall chlorate level in the bulk milk tank may depend on the level of chlorate in the water, the volume of water entering the milk and the volume of milk being adulterated with water (containing chlorate). In the current study, chlorate was only detected in milk sampled from the first row of cows milked. Therefore, the proportion of milk in the bulk tank that is supplied *via* the first row of cows milked will likely dictate the overall bulk milk tank chlorate level. A similar pattern of contamination was displayed by Ryan *et al*. (2012) where TCM levels were higher in milk sampled at the start of milking *versus* that sampled mid-way through milking. Furthermore, stage of lactation may also impact bulk tank chlorate levels due to lower dilution when lower volumes of milk are produced in both early and late lactation (Paludetti *et al*. 2019; Gleeson *et al*. 2022).

It could be suggested that bacteria present within the raw milk in both the laboratory and field studies resulted in degradation of at least some of the chlorate present (McCarthy *et al*. 2023) and that this may have influenced the chlorate levels detected in milk and ultimately the outcomes of the experiments. However, in both studies, total bacterial counts are of a good standard as both were within regulatory limits (Gleeson *et al*. 2013) and therefore, it is unlikely that bacterial degradation of chlorate occurred and influenced the outcomes of this research.

## CONCLUSION

Increased levels of chlorate in water were associated with increased levels of chlorine being added to water. Using an ‘aged’ *versus* ‘fresh’ chlorination agent, that is, sodium hypochlorite also resulted in increased chlorate levels in water. At laboratory scale, chlorate levels increased numerically in milk following spiking with water containing increasing levels of chlorate. Regarding the field experiment, the adulteration of milk with water (containing chlorate) that had not drained from the milking plant pre-milking resulted in chlorate contamination of milk. Therefore, to minimise the effect that chlorinated water may have on milk produced on farms, thorough drainage of milk handling equipment, that is, the milking plant and the bulk tank is vital.

## ACKNOWLEDGEMENTS

The authors would like to acknowledge Dr Phoebe Hartnett for assisting with the laboratory experiment, Dr Mary Moloney, Dr Moses Madende and Dr Martin Danaher for the quantification of chlorate, Paula Reid for assisting with statistical analysis and Jim Flynn for conducting milk freezing point analysis. Open access funding provided by IReL.

## AUTHOR CONTRIBUTIONS

**L Twomey:** Methodology; writing – original draft; writing – review and editing; formal analysis; data curation; investigation. **Ambrose Furey:** Writing – review and editing; supervision. **Bernadette O’Brien:** Conceptualization; funding acquisition; writing – review and editing; project administration; supervision; methodology. **Tom Beresford:** Conceptualization; writing – review and editing; project administration; supervision; methodology. **David Gleeson:** Conceptualization; funding acquisition; writing – review and editing; project administration; supervision; methodology.



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## CONFLICT OF INTEREST

The authors declare that there are no conflicts of interest associated with this article.

## FUNDING INFORMATION

This research was funded by both the Irish Department of Agriculture, Food and Marine (DAFM) as part of the Food Institutional Research Measure (FIRM); Grant number 2019R555 and through Dairy Research Ireland (Project number 1163). Lorna Twomey is also in receipt of a Teagasc Walsh Scholarship funded by the DAFM (FIRM) grant.

## DATA AVAILABILITY STATEMENT

Research data are not shared.

## REFERENCES

Alfredo K, Stanford B, Roberson J A and Eaton A (2015) Chlorate challenges for water systems. *Journal-American Water Works Association* **107** 187–196.

Asami M, Yoshida N, Kosaka K, Ohno K and Matsui Y (2013) Contribution of tap water to chlorate and perchlorate intake: A market basket study. *Science of the Total Environment* **463** 199–208.

Bord Bia (2020) *Dairy from Ireland: Where We Work in Harmony with Nature*. Dublin: Bord Bia - Irish Food Bord. www.bordbia.info/dairy/. Accessed 22/6/2023.

Breytus A, Kruzic A P and Prabakar S (2017) Chlorine decay and chlorate formation in two water treatment facilities. *Journal-American Water Works Association* **109** 110–120.

Commission EU (2020) COMMISSION REGULATION (EU) 2020/749 of 4 June 2020 amending annex III to Regulation (EC) No 396/2005 of the European Parliament and of the council as regards maximum residue levels for chlorate in or on certain products. *Journal of the European Union* **178** 7–20.

Council EU (2020) Directive (EU) 2020/2184 of the European parliament and of the council of 16 December 2020 on the quality of water intended for human consumption (recast). *Journal of the European Union* **435** 1–62.

Environmental Protection Agency (2011) *Water Treatment Manual: Disinfection*. Wexford: Environmental Protection Agency. www.epa.ie/publications/compliance--enforcement/drinking-water/advice--guidance/epa-water-treatment-manual-filtration.php. Accessed 1/6/2023.

Gleeson D (2016) *Chlorates in Milk: sample results to date*. Fermoy: Teagasc. www.teagasc.ie/media/website/animals/dairy/Chlorates-in-Milk-David-Gleeson.pdf. Accessed 14/7/2023.

Gleeson D, O'Connell A and Jordan K (2013) Review of potential sources and control of thermoduric bacteria in bulk-tank milk. *Irish Journal of Agricultural and Food Research* **52** 217–227.

Gleeson D, Paludetti L, O'Brien B and Beresford T (2022) Effect of 'chlorine-free'cleaning of milking equipment on the microbiological quality and chlorine-related residues in bulk tank milk. *International Journal of Dairy Technology* **75** 262–269.

Gordon G, Adam L C, Bubnis B P, Kuo C, Cushing R S and Sakaji R H (1997) Predicting liquid bleach decomposition. *Journal-American Water Works Association* **89** 142–149.

Industrial Test Systems Incorporated (2019) *Dual Wavelength Advanced Photometer System Instruction Manual*. Rock Hill, SC: Industrial Test Systems Incorporated.

Irish Milk Quality Co-operative Society (2009) *Teagasc/IMQCS Recommendations for the Installation and Testing of Milking Machines*. Dublin: Irish Milk Quality Co-operative Society. www.milkquality.ie/documents/Teagasc_IMQCS_Manual.pdf. Accessed 14/7/2023.

Irish Water (2021) Drinking Water Parameters. [Internet document] URL www.water.ie/water-supply/water-quality/parameters/. Accessed 9/3/2021.

Kettlitz B, Kemendi G, Thorgrimsson N, Cattoor N, Verzegnassi L, Le Bail-Collet Y, Maphosa F, Perrichet A, Christall B and Stadler R H (2016) Why chlorate occurs in potable water and processed foods: A critical assessment and challenges faced by the food industry. *Food Additives & Contaminants: Part A* **33** 968–982.

Kriem L S (2017) *Chlorate Formation in on-Site Hypochlorite Generation Facilities: Effects of Temperature, pH and Storage Times*. Master Thesis, Michigan: Michigan State University.

Laird D T, Gambrel-Lenarz S A, Scher F M and Reddy R (2004) Microbiological count methods. In *Standard Methods for the Examination of Dairy Products*, pp. 153–186. Wehr H M and Frank J F, eds. Washington, DC: American Public Health Association.

McCarthy W P, O'Callaghan T F, Danahar M, Gleeson D, O'Connor C, Fenelon M A and Tobin J T (2018) Chlorate and other oxychlorine contaminants within the dairy supply chain. *Comprehensive Reviews in Food Science and Food Safety* **17** 1561–1575.

McCarthy W P, Srinivas M, Danaher M, O'Connor C, O'Callaghan T F, van Sinderen D, Kenny J and Tobin J T (2023) Isolation and identification of chlorate-reducing hafnia sp. from milk. *Microbiology* **169** 1–9.

Moloney M, Hossain M and Danaher M (2021) Teagasc accredited method SOP FADM 530: Determination of oxyanion residues in dairy products by UHPLC-MS/MS. Teagasc food research Centre Ashtown Dublin 15 (version 3.0, 16/02/2021).

National Federation of Group Water Schemes (2017) *Chlorination: Information for Group Water Schemes*. Monaghan: National Federation of Group Water Schemes. www.nfgws.ie/chlorination/. Accessed 26/1/2021.

Nobile M, Danesi L, Pavlovic R, Mosconi G, Di Cesare F, Arioli F, Villa R, Chiesa L M and Panseri S (2022) Presence of chlorate and perchlorate residues in raw bovine milk from Italian farms. *Food* **11** 1–9.

O'Connell A, Ruegg P L, Jordan K, O'Brien B and Gleeson D (2016) The effect of storage temperature and duration on the microbial quality of bulk tank milk. *Journal of Dairy Science* **99** 3367–3374.

Paludetti L F, Kelly A L, O'Brien B and Gleeson D (2019) Monitoring residue concentrations in milk from farm and throughout a milk powder manufacturing process. *Journal of Dairy Research* **86** 341–346.

Phelan S (2019) Ornua moves to phase out chlorine-based detergents. *Agriland*. www.agriland.ie/farming-news/ornua-moves-to-phase-out-chlorine-based-detergents/. Accessed 1/9/2021.

Rao B, Hatzinger P B, Böhlke J K, Sturchio N C, Andraski B J, Eckardt F D and Jackson W A (2010) Natural chlorate in the environment: Application of a new IC-ESI/MS/MS method with a Cl18O3-internal standard. *Environmental Science & Technology* **44** 8429–8434.

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Ryan T and Donworth J (2016) Milking facilities. In *Teagasc Dairy Manual*, pp. 225–238. Carlow: Teagasc. www.teagasc.ie/media/website/publications/2016/Dairy-Manual-Section3.pdf. Accessed 14/7/2023.

Ryan S, Gleeson D, Jordan K, Furey A and O'Brien B (2012) Evaluation of trichloromethane formation from chlorine-based cleaning and disinfection agents in cow's milk. *International Journal of Dairy Technology* **65** 498–502.

Stanford B D, Pisarenko A N, Snyder S A and Gordon G (2011) Perchlorate, bromate, and chlorate in hypochlorite solutions: Guidelines for utilities. *Journal-American Water Works Association* **103** 71–83.

Twomey L, Gleeson D and Furey A (2023) Investigating the Effect that Chlorinated Water has on Chlorate Levels in Bulk Milk. A presentation at the Teagasc Milk Quality Workshop. [Internet document] URL www.teagasc.ie/media/website/animals/dairy/3.-Chlorate-levels-in-water-and-its-impact-on-milk-residues_LTowmey.pdf. Accessed 14/2/2023.

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