# Investigating the Effect that Chlorinated Water has on Chlorate Levels in Bulk Milk

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WALSH SCHOLARSHIPS PROGRAMME

Agriculture and Food Development Authority

An Roinn Talmhaíochta, Bia agus Mara
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# Introduction

Many farms use chlorinated water; most usually sourced from public or group schemes to clean their milking equipment.

It is widely suggested that where chlorinated water is used for rinsing milking equipment; it can result in chlorate residue in milk.

In order to investigate this theory both **laboratory** and **field based trials** were conducted; the objectives of which were to;

- **Investigate the occurrence of chlorate in water containing different levels of total chlorine.**
- **Investigate the occurrence of chlorate in milk as a result of contact with chlorinated water.**
- **Establish if chlorinated water containing chlorate has the capacity to contaminate milk with chlorate when used to rinse a milking machine pre – milking.**
- **Establish if rinsing the plant with chlorinated water + peracetic acid eliminates the occurrence of chlorate residue in milk at detectable levels.**

# Context of Study

## Water sources on commercial dairy farms

Of the first 60 farms visited as part of the 2022 farm study;

40 had their own private well;

- 14 of these wells displayed detectable levels of chlorate with a mean level of 0.02 mg/L.

16 farms were supplied by Irish Water;

- 12 of these displayed detectable levels of chlorate with a mean level of 0.17 mg/L.

3 farms were supplied by private group water schemes;

- Chlorate was detected in water taken from each of these farms with a mean level of 0.16 mg/L.

Chlorate was still detected in untreated wells; but at levels far lower than in chlorinated water supplies.

# Laboratory Experiment

## Establishing the Effect that Water Total Chlorine Level and Sodium Hypochlorite Age Have on the Level of Chlorate Detected in Water

### Why conduct this experiment?

As chlorinated water supplies are not universal across the country and vary in terms of total chlorine content and chlorination agent age the effect that both of these variables have on chlorate levels in water must be investigated.

### Objectives

- Establish the relationship between total chlorine levels in water and chlorate levels in water.
- Establish the impact that aging of sodium hypochlorite has on the chlorate levels in water.

**Total chlorine:** free chlorine + sequestered chlorine.

### Six Treatments (Target Total Chlorine Levels)

- Control (non-chlorinated water)
- 0.50 mg/L
- 1.00 mg/L
- 1.50 mg/L
- 2.00 mg/L
- 2.50 mg/L

Treatments are based on typical total chlorine levels utilised by Irish Water.

### Sodium Hypochlorite used at four time points over its 6 month useful life; termed 'phases'

- Phase One - 0 days old NaClO
- Phase Two - 62 days old NaClO
- Phase Three - 119 days old NaClO
- Phase Four - 175 days old NaClO

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# Materials & Methods

Chlorine free well water was chlorinated as part of this experiment.

A TBC test was conducted on the well water at each phase to deduce its bacterial quality (all waters were ≤100 cfu/ml).

Well water was taken from the same source for all four ‘phases’ of the experiment and was sourced on the morning of each ‘phase’ and refrigerated until required.

Treatments were created in glass Duran bottles and were 500ml in volume.

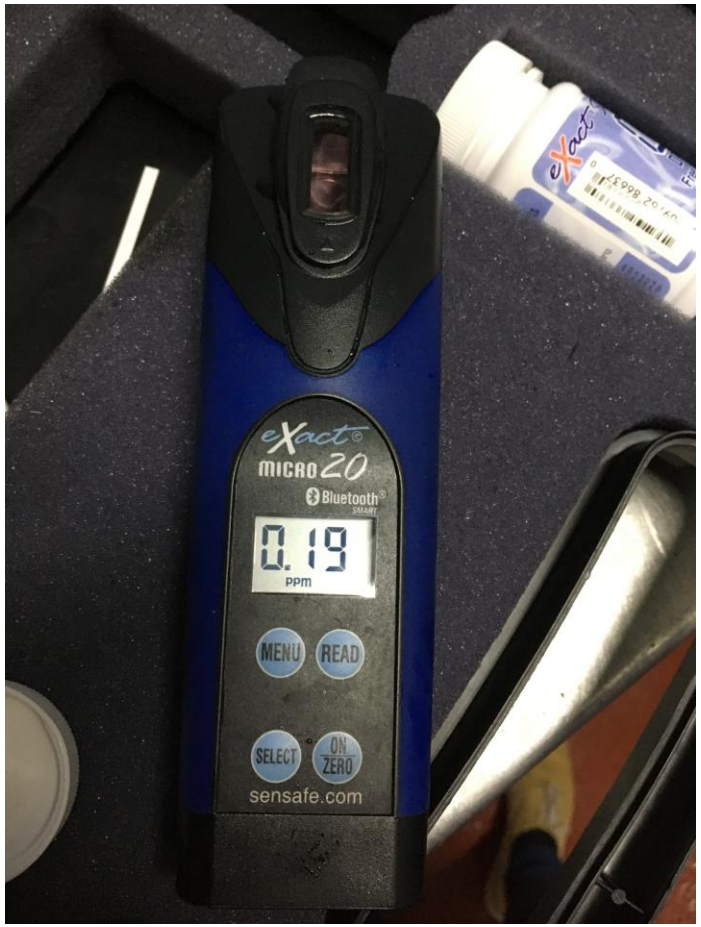
Treatments were created using 100 mg/L standard solutions;

- 1 gram of hypochlorite was added to 1,000ml of well water.
- Predetermined volumes of this standard solution were then dosed into 500ml of well water to create each treatment.

All treatments were tested for total & free chlorine in duplicate.

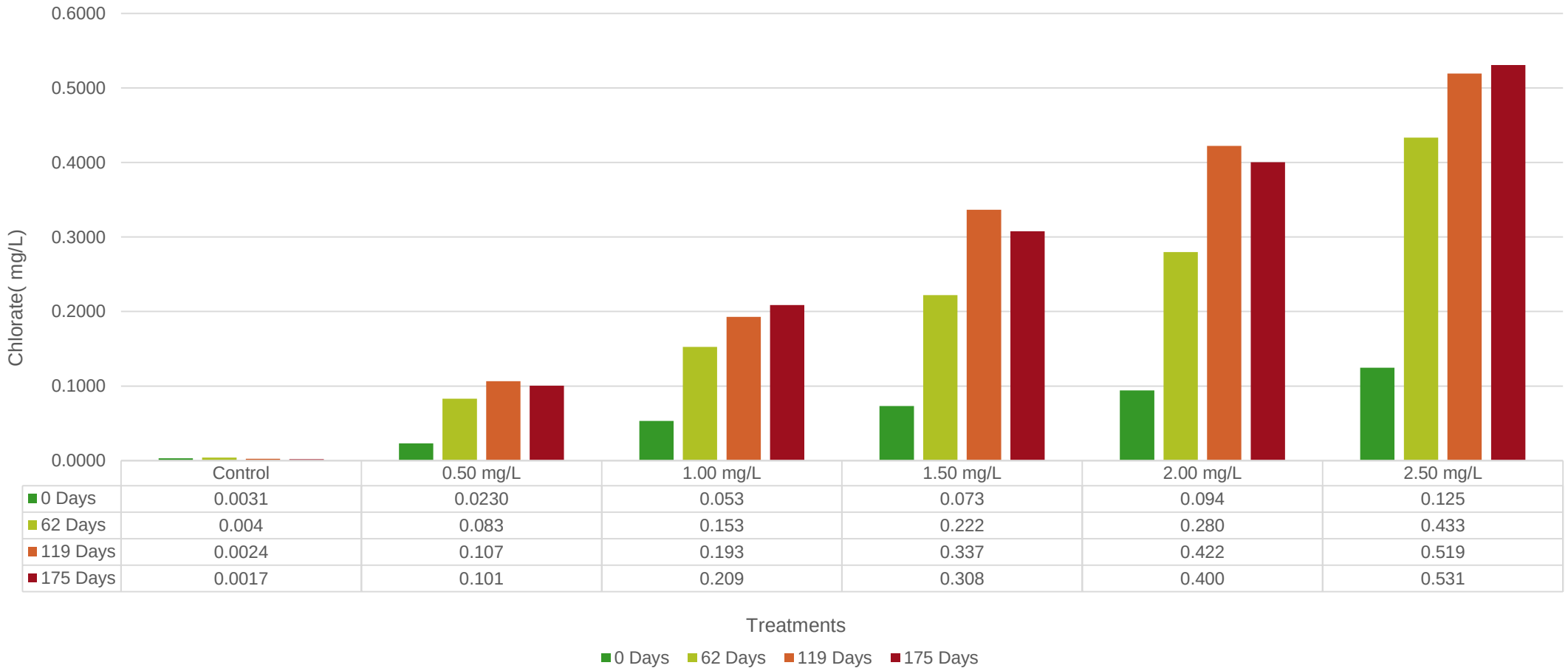
**The sodium hypochlorite was stored as per manufacturers recommendations and sub-sampled into an opaque sample tube after inversion for use in this experiment.**

Waters were analysed for chlorate using UPLC – MS/MS in Teagasc, Ashtown at a minimum level of detection of **0.0002 mg/L**.



# Laboratory Trial

## Chlorate Levels in Well Waters Over a 6 Month Chlorination Period




| | Control | 0.50 mg/L | 1.00 mg/L | 1.50 mg/L | 2.00 mg/L | 2.50 mg/L |
|---|---|---|---|---|---|---|
| 0 Days | 0.0031 | 0.0230 | 0.053 | 0.073 | 0.094 | 0.125 |
| 62 Days | 0.004 | 0.083 | 0.153 | 0.222 | 0.280 | 0.433 |
| 119 Days | 0.0024 | 0.107 | 0.193 | 0.337 | 0.422 | 0.519 |
| 175 Days | 0.0017 | 0.101 | 0.209 | 0.308 | 0.400 | 0.531 |

Both total chlorine level and sodium hypochlorite age influence chlorate levels in chlorinated water;

- Higher total chlorine levels and older hypochlorite predispose higher levels of chlorate in water.

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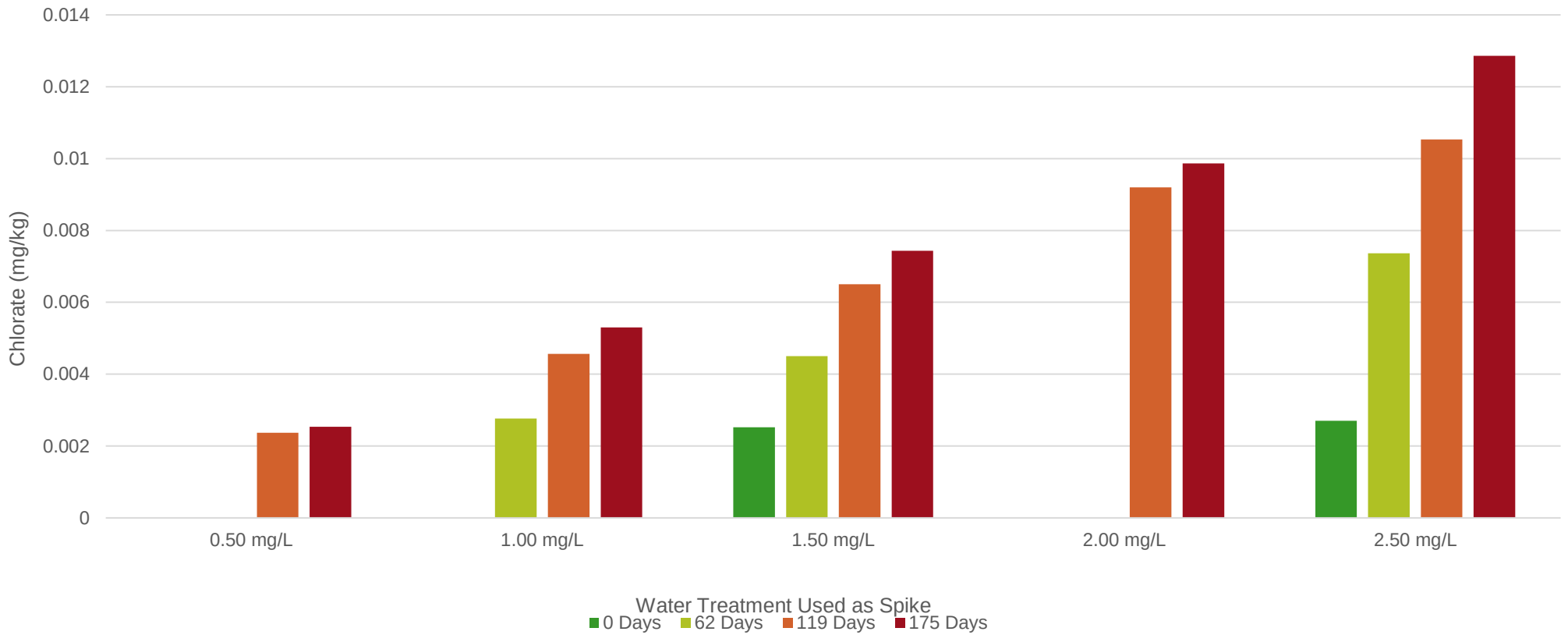
# Establishing the Effect that Water Containing Chlorate has on Chlorate Levels in Milk

## How was this done?

- Chlorinated well waters from each of the four ‘phases’ of the lab water experiment were retained in a frozen state.
- Waters from all four ‘phases’ were defrosted in the fridge overnight and 4 litres of milk was sourced from the Moorepark bulk tank.
- This milk was divided into 24 x 100ml portions – 6 x spiking treatments in each of the 4 phases.
- Each 100ml portion of milk was spiked at a rate of 2% and thoroughly mixed and then 3 x 25ml aliquots were taken to allow for analysis of chlorate in triplicate for each spiked milk.
- Samples were frozen at -20 C ASAP after spiking and tested for chlorate at Teagasc Ashtown.

# Laboratory Trial

## Chlorate Levels in Milks Spiked with Waters Chlorinated over a 6 month Period




- Chlorate in water can result in chlorate in milk after direct contact between water and milk.
- The greater the level of chlorate in the water; the greater the level of chlorate that can be expected in the milk.

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# Conclusions - Laboratory Trial

- Water containing greater levels of total chlorine will contain greater levels of chlorate.
- Using aged sodium hypochlorite to chlorinate water will result in greater levels of chlorate in water;
  - Using aged sodium hypochlorite to chlorinate water at high levels will result in high levels of chlorate in water.
- Where water with increasing levels of chlorate enters milk; increasing level of chlorate will be detected in said milk.
- This laboratory based trial suggests that waters with higher levels of total chlorine and the use of aged sodium hypochlorite are the biggest risk factors for chlorate occurrence.
  - Therefore, posing the greatest threat to milk.

# Field Trial
# Materials & Methods

- A rinsing trial was conducted on the 30 unit swing over milking parlour in Moorepark in November/ December 2021.

- 4 x rinsing treatments were applied in a random order;
  1. Final rinse in a chlorinated water + a 0.1% peracetic acid solution (control treatment)
  2. Final rinse in water containing 0.10 mg/L of chlorine
  3. Final rinse in water containing 0.50 mg/L of chorine
  4. Final rinse in water containing 2.00 mg/L of chlorine

- Each treatment was applied 3 times; in random order and within 2 hours of milking beginning.

- Treatments 2, 3 & 4 were applied after the standard wash routine had taken place.

- **0.10 mg/L –** lowest level of chlorine found in public water supplies.
- **0.50 mg/L –** typical level of chlorine found in public water supplies.
- **2.00 mg/L –** highest level of chlorine permitted in public water supplies at the point of consumption.

# Materials & Methods
## Applying the chlorinated water rinses

**Standard CF wash routine is applied post milking;**

- Post milking rinse (12 litres/ unit)
- Hot chlorine free wash (9 litres/ unit)
- Post detergent rinse (12 litres/ unit)
- Additional 0.1% peracetic acid rinse (12 litres/ unit)

**Chlorinated water rinse**

- 360 litres of chlorinated water (12 litres/ unit) was used to rinse the plant in advance of afternoon milking.
- Rinsing the plant took 7.5 minutes and just under 2 minutes to drain and purge as much residual water from the line as possible.
- An automatic valve drained as much water from the receiver vessel as possible before milking commenced.

# Materials & Methods – Water Sampling

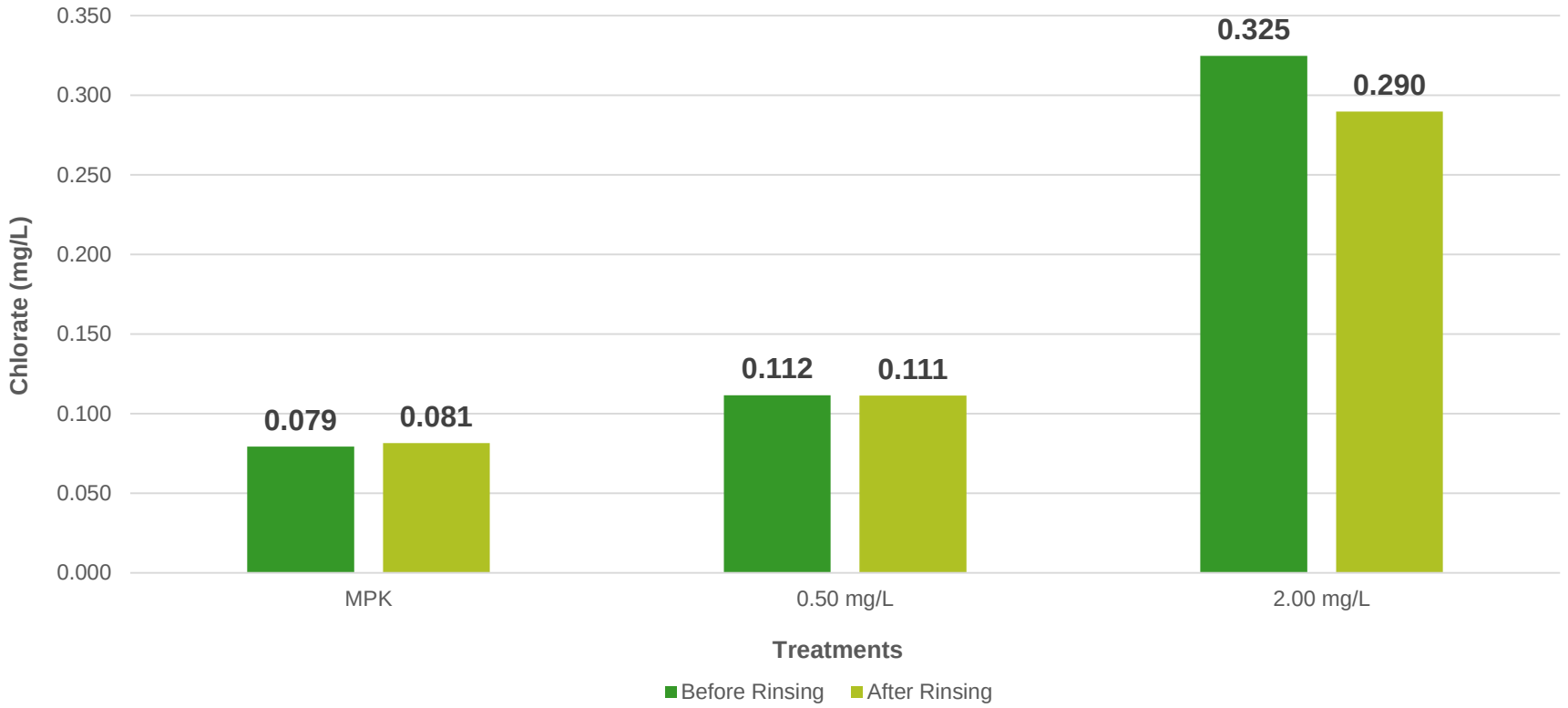
- 3 x 50ml samples of the rinse water were taken from the trough pre-rinsing using sterile dippers and were tested for both chlorine (in-situ) and chlorate levels.

- During the rinse cycle 3 x 50ml samples of water were taken from the in-line sampling tap; one each at;
  - When 200 seconds of the rinse cycle remained
  - When 100 seconds of the rinse cycle remained
  - When 10 seconds of the purge phase remained.

**The premise of this was to determine if chlorate levels changed during the rinse.**

- Each sample was tested for both chlorine and chlorate levels.

# Dynamics of Chlorate Levels in Water Before & After Rinsing




- The higher the chlorine level of the water the more chlorate present in it; correlates with laboratory findings.
- The water that went into and came out of the plant was virtually the same in terms of chlorate content.
  - Therefore, there is no evidence of chlorate deposition in the milking plant independent of water.

# Materials & Methods – Milk Sampling

- 300ml in-line samples of milk were taken when clusters were attached to all 30 cows in the first row and was taken before the milk entered the milk filter and plate cooler - the same was done for rows 2 and 3.
  - The sample taken when all 30 cows were milking also represented the very first milk to be pumped through the line.

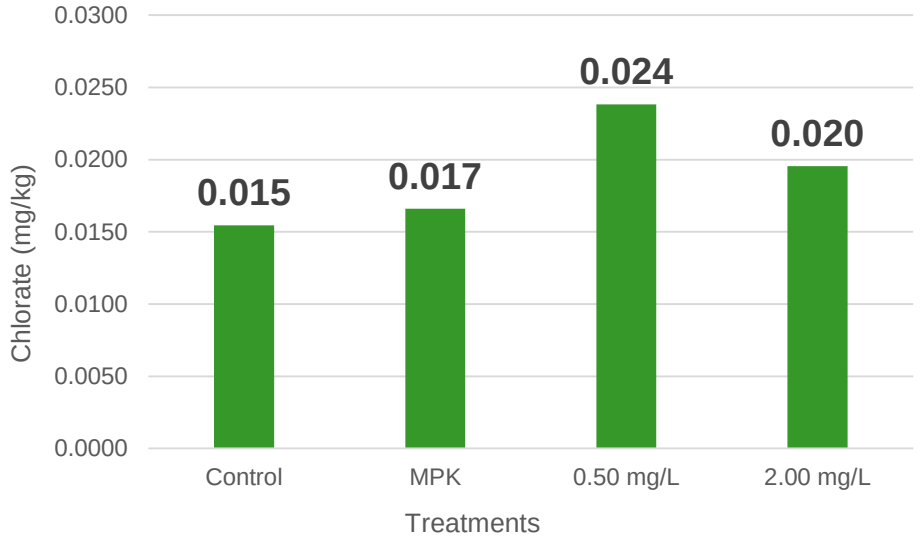
- Each 300ml milk sample was aliquoted into 6 x 25ml portions; 3 being tested for chlorate and 3 being tested for their FPD.

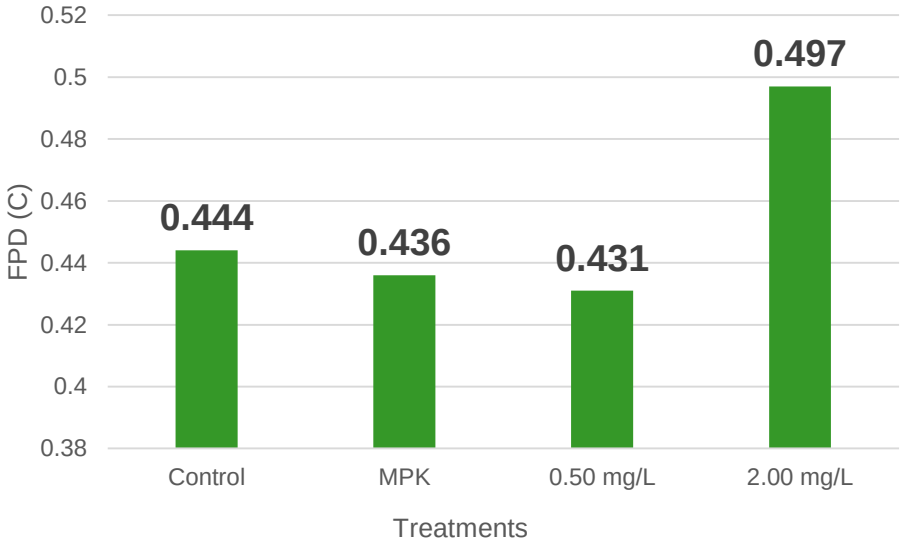
- Milks were kept on ice at all times until they were placed in the freezer (both chlorate & FPD samples).

- Both water and milk samples were analysed for chlorate using UPLC – MS/MS at Teagasc, Ashtown.

- Milk samples were analysed for FPD using a Milkoscan 7 at Teagasc, Moorepark.

# Chlorate & FPD Results for Row 1 Milks




- Chlorate was detected in milk sampled from row 1, but <u>not detected in milks from rows 2 or 3</u> and this was consistent across all treatments.
- The detection of higher levels of chlorate was not dependent upon higher levels of chlorine and by association, chlorate in the rinse water.
- Instead, the detection of chlorate in row 1 milk coincided with the presence of extraneous water; FPD values of < 0.500°C.
- As the presence of chlorate at detectable levels coincided with extraneous water in row 1 milks it can be concluded that the water content of the milk dictated the presence of chlorate.

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# Are the outcomes of this field experiment reflected by chlorate levels in both waters and milks from commercial dairy farms?

| Chlorate in Water (mg/L) | Water Source | Chlorate in Milk (mg/kg) |
|---|---|---|
| 0.396 | Well + Irish Water | <0.0020 |
| 0.386 | Irish Water | <0.0020 |
| 0.37 | Private Group Scheme | 0.0023 |
| 0.364 | Irish Water | <0.0020 |
| 0.222 | Irish Water | <0.0020 |
| 0.167 | Irish Water | <0.0020 |
| 0.133 | Irish Water | <0.0020 |
| 0.119 | Well | <0.0020 |
| 0.106 | Irish Water | <0.0020 |
| 0.105 | Well | <0.0020 |

***The table presents the 10 highest waters in terms of their chlorate levels and the corresponding milk result (top 10 of the first 60 waters/ milks analysed from 2022 farm visits).***

Only one of the ten farms had a detectable level of chlorate in the milk confirming that it requires more than simply using chlorinated water for cleaning that can lead to chlorate in milk.

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# Conclusions

**Based on the outcomes of this experiment it can be concluded that;**

- Using chlorinated water to rinse a milking machine before milking begins will likely result in chlorate being present in milk produced by the first row of cows only.
- Milk yielded from subsequent rows of cows is unlikely to be contaminated with chlorate regardless of water total chlorine content.
- Chlorate contamination of row 1 milk is a consequence of extraneous water [containing chlorate] in the milk and not of chlorate residue deposited onto the milking plant during rinsing.
- As the presence of extraneous water dictates the likelihood of chlorate contamination in milk, as opposed to the chlorate content of the water, **it is not correct to assume that water containing higher levels of chlorate will result in greater levels of chlorate contamination of milk**.
    - This is substantiated by chlorate levels in milks taken from dairy farms with elevated levels of chlorate in water.

# Conclusions

- The inclusion of peracetic acid (0.1%) in the final rinse water did not eliminate chlorate residue in row 1 milk [control treatment – MPK wash routine].

- The impact that chlorate in row 1 milk has on overall bulk tank milk chlorate levels will greatly depend on the level of chlorate in row 1 milk, the final volume of milk at collection and the associated dilution effect.

- Therefore, a possible stage of lactation effect exists where bulk milk may be at greater risk of displaying detected levels of chlorate during early and late lactation when milk volumes are lower; where row 1 milk has been contaminated with chlorate.

- Taking steps to minimize the amount of extraneous water that enters the milk produced by the first row of cows, may be necessary on farms using chlorinated water for milking machine rinsing.

# Necessary Steps to Minimize Chlorinated Water Entering Milk

The key thing when it comes to chlorinated water causing chlorate contamination of bulk milk is **MILKING EQUIPMENT DRAINAGE**

Ensure that likely areas for water retention are drained properly pre-milking;

- Receiver vessel
- Milk filter housing
- Clusters and long milk tubes
- Bulk tank – post washing (inspect the cleaned tank regularly for sitting water)

This may mean installing automatic drainage valves and/ or changing your routine practices slightly.

Ensure that the milk transfer pipe is disconnected from the bulk tank before rinsing begins.

**Be particularly cognisant of the need for these steps when milk volumes are low and where chlorate levels are known to be/ likely to be very high.**

**Drainage** **Drainage**

**Drainage**

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# Thank you

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