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## Minimizing Risks: Use of Surface Water in Pre-Harvest Agricultural Irrigation; Part II: Sodium and Calcium Hypochlorite (Chlorine) Treatment Methods

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### What is chlorine?

Chlorine is a water-soluble chemical disinfectant that is commonly used for microbial disinfection because it is effective, economical, and approved by the Environmental Protection Agency (EPA) for water treatment (EPA, 2017). Chlorine-based compounds have been used as 'primary' disinfectants for drinking water, wastewater, and agricultural irrigation water (Figure 1) for decades. Primary disinfection kills or inactivates bacteria, viruses, and other potentially harmful organisms. Chlorine is also an effective 'secondary' disinfectant for prevention of bacterial and fungal growth or re-growth in distribution systems. Secondary disinfection provides long-lasting, residual water treatment as the water moves through pipes, including irrigation pipes and sprinklers with prolonged retention times (Schwankl et al., 2012). In general, chlorine can be applied to irrigation water in three forms: (1) as solid calcium hypochlorite [Ca(OCl)<sub>2</sub>], (2) as liquid sodium hypochlorite (NaOCl, or common bleach), or (3) as gaseous chlorine (Cl<sub>2</sub>) (USDA NRCS; Schwankl et



Figure 1. Chlorine treatment for agricultural irrigation. Image credit Jessica Dery, UA.

al., 2012). **Table 1** provides a brief overview of these three forms of chlorine. Each form varies in concentrations of 'available' chlorine, levels of effectiveness, characteristics, and advantages. It is therefore important to understand

Form	Action when added to water	Available chlorine	Points of interest
Gaseous Chlorine (Cl <sub>2</sub> )	Decreases pH and alkalinity	100%	<ul> <li>Most hazardous (poisonous and corrosive)</li> <li>Extensive training required</li> <li>May be preferred in alkaline waters because it decreases pH</li> </ul>
Solid calcium nypochlorite (Ca(OCl) <sub>2</sub> )	Increases pH, hardness, and alkalinity	65-75%	<ul> <li>Not recommended for injection into drip irrigation (calcium precipitates may clog emitters)</li> <li>Less corrosive than liquid form</li> <li>Less stable in normal storage conditions</li> </ul>
Liquid sodium hypochlorite (NaOCI)	Increases pH and alkalinity	10-15%	<ul> <li>Easy to use</li> <li>Generally safe to use</li> <li>No special training required</li> <li>Should be stored in a shaded area and away from fertilizers</li> <li>Degrades over time</li> </ul>

Table 1. Overview of three forms of chlorine available for disinfection of water.

these differences before deciding on a chlorine treatment method for your agricultural irrigation water.

# **Key Points:**

- Chlorine efficacy depends on pH:
  - Solid and liquid chlorine act as bases that can increase the pH of irrigation water.
  - Free chlorine is most effective at pH 6.0-7.5, where [HOCl] > [OCl<sup>-</sup>].
  - Chlorination may require pH adjustment via acid addition.
- Chlorine efficacy depends on nitrogen content of irrigation water:
  - Use of fertilizers, herbicides, and insecticides can result in combined chlorine.
  - Combined chlorine is less effective than free chlorine.
  - Direct reactions between fertilizers and chlorine can also be hazardous.
- Chlorine efficacy depends on temperature:
  - Disinfection is more effective at higher temperatures.
  - Higher temperatures can also increase chlorine demand.
- Follow all label directions to prevent injuries and wear personal protective equipment (PPE) when handling any chemicals.

- Always add chlorine to water when making stock solution (not water to chlorine).
- Do not mix acid and chlorine directly (to avoid toxic chlorine gas).
- Use different injection ports that are at least 2-3 feet away from each other.
- Target free chlorine residual (1-2 ppm) should be measured at the furthest point (last head) in the irrigation system (EPA, 2014).

## What does chlorine treat?

Chlorine can be used to treat pathogenic, or diseasecausing, microorganisms as well as indicator microorganisms in water that are important in fresh produce safety. **Tables 2 and 3** provide information on inactivating human and plant pathogens using chlorine. Chlorine is particularly effective against bacteria and viruses but is less effective against protozoa and fungi. When chlorine contacts a microbial cell, it begins to break down the cell wall by creating lesions. These lesions or 'holes' affect critical cellular functions of the microorganisms, such as respiration, and thus the organism is inactivated or killed (WHO, 2004). Some bacteria of concern to agricultural professionals, such as *Escherichia coli* (*E. coli*), *Salmonella*, and *Campylobacter*, can be destroyed quickly upon contact (seconds to minutes),

Table 2 Inactivation h	w chlorine treatmer	it of nathonene	significant to human health.
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Pathogen	From WHO guidelines (Drinking Water)				Concentration of chlorine	Time of chlorine	Ct value	Inactivation
	Health significance	Persistence in water	Tolerance to chlorine	Relative infectivity	(ppm)	Exposure (min)	(mg-min/L)	(%)
Bacteria: Huma	n pathogen	11		1	I		1	1
Campylobacter jejuni²	High	Moderate	Low	Moderate	0.1	5	0.5	99-99.9%
Escherichia coli <sup>7</sup>	High	Moderate	Low	Low	0.5	<0.5	<0.25	99.99%
E. coli (entero- hemorrhagic) <sup>7</sup>	High	Moderate	Low	High	0.5	<0.5	<0.25	99.98-99.99%
Salmonella typhi <sup>3</sup>	High	Moderate	Low	Low	0.05	20	1	99.2%
Protozoa: Humar	n pathogen						1	
*Cryptosporidium parvum <sup>6</sup>	High	Long	High	High	80	90	7200⁵	99.9%

\**Cryptosporidium* oocysts are highly resistant to chlorine disinfection and should be used in conjunction with other treatment methods. *Cyclospora cayetanensis*, another protozoan of public health concern in fresh produce, shares similar characteristics and is also highly resistant to chlorine.

Table 3. Inactivation by chlorine treatment of pathogens significant to plant health

Pathogen	Disease	Persistence in soil	Tolerance to chlorine	Concentration of chlorine (ppm)	Time of chlorine exposure (min)	Ct value (mg-min/L)	Inactivation (%)
Fungus: Plant	pathogen						
Fusarium oxysporum (conidia)	Wilt	Indefinitely	High	14	6	84	Not detectable
<i>Rhizoctonia solan</i> i (mycelia)	Leaf drop	Indefinitely	High	12	10	120	Not detectable
Sources: Kerns, D.L. e	ources: Kerns, D.L. et al., 1999; Cayanan, D. F. et al. 2009						

while spore-forming bacteria or the cysts/oocysts of protozoa, as well as some fungi (e.g., *Fusarium*), are more resistant to chlorine and can take longer to be killed (minutes to hours) (WHO, 2004). In addition to targeting specific microorganisms, chlorine can also be used to reduce or eliminate biofilm growth (i.e., biofouling caused by groups of organisms), which is often responsible for clogged emitters or sprinkler heads (Schwankl et al., 2012).

# What happens when chlorine is added to irrigation water?

When chlorine is added to irrigation water, chemical reactions with water, inorganic matter, and organic matter occur very quickly. During reactions with water, chlorine primarily forms two compounds or 'species': hypochlorous acid (HOCl) and hypochlorite ion (OCl<sup>-</sup>). Both are capable of disinfection, but HOCl can be 40 to 80 times stronger than OCl<sup>-</sup> (Meador et al., 2013). **Figure 2** shows the distribution of three chlorine species in aqueous solution, based on the pH of the water.

After the initial reactions with water, HOCl and OCl<sup>-</sup>then react with inorganic (e.g., ammonia) and organic (e.g., urea) compounds found in the water. During these secondary reactions, the chlorine is converted to combined chlorine with less disinfecting power or is consumed and is no longer available for disinfection. This initial consumption is based on a property of water called the **chlorine demand**. The chlorine demand of irrigation water fluctuates over time (EPA, 2017) and depends on the amount of organic matter (and other oxidizable substances), the applied chlorine dose, temperature, and pH. Drinking water from your tap at home will generally have a low chlorine demand because it has already been treated and contains very little organic and inorganic material for the chlorine to react with. On the other hand, open irrigation canals, lakes, and rivers are susceptible to varying environmental conditions and inputs from wildlife and humans and therefore can contain higher concentrations of organic and inorganic material. These waters are also subject to increased loads of ammonia, nitrites, and nitrates during fertigation.



At pH 7.5:
HOCl and ClO<sup>-</sup> are in chemical equilibrium (50:50)
Preferred form for disinfection:

HOCl

Ideal pH for disinfection:

6 - 7.5

At pH below 7.5:

Corrosivity can occur



Recycled water may also have higher chlorine demand due to its higher concentration of organic matter (Zheng et al., 2008). Any HOCl and OCl<sup>-</sup> that remains after the initial reactions make up what is called **free available chlorine** (USDA NRCS). The sum of combined chlorine and free chlorine at any time is called the **total chlorine residual**.

Applied Chlorine Dose = Free Chlorine + Combined Chlorine + Chlorine Demand

Total Chlorine Residual = Free Chlorine + Combined Chlorine

Chlorine Demand = Applied Chlorine Dose – Total Chlorine Residual

# How are pathogens controlled using chlorine?

The best practice for controlling pathogens in water with chlorine is to maintain a certain level of free chlorine for a specified contact time (Zheng et al., 2008). The free chlorine 'CT' value is determined by multiplying the concentration of disinfectant (C in ppm or mg/L) by the contact time (T in minutes) and is commonly known as the free chlorine 'CT' value. It is often expressed as mg-min/L. This value can be compared to known pathogen disinfection rates to estimate the efficacy of a certain disinfectant or dose (Tables 2 and 3). Chlorine should maintain a sufficient contact time with microorganisms within all parts of the irrigation system to be effective. In most cases, a chlorine dose of 5 to 6 ppm will usually be sufficient to achieve a free chlorine residual of between 1 to 2 ppm (USDA NRCS) at the point of irrigation. However, it is recommended that if using chlorine as a primary disinfectant in irrigation water, that the appropriate amount of residual chlorine be validated against the desired reduction in microbiological concentration in the water, in accordance with irrigation water quality guidelines (e.g. LGMA, FSMA, or other customer requirements).

When adding chlorine to a water source, there is a point where the total chlorine residual drops suddenly (points B to C in Figure 3) — an indication that the system is approaching **breakpoint chlorination** (point C in **Figure 3**). It is at this point where any additional applied chlorine will become free available chlorine. It is important to make note of breakpoint chlorination, because only after this point will there be free chlorine available to disinfect microbes in the irrigation water.



Figure 3. Chlorine demand and breakpoint chlorination.

# What factors influence the effectiveness of chlorine?

The effectiveness of chlorine is influenced by several factors such as the applied dose, temperature, water quality (e.g., pH, turbidity, and organic matter), contact time, and target microbe characteristics (Figure 4). Disinfection generally occurs more rapidly at higher temperatures, but higher temperatures can also increase reactivity with non-target materials, thereby increasing chlorine demand. Chlorine disinfection is most effective at temperatures between 65°F (18°C) up to 99°F (37°C), but free chlorine residual should be verified, particularly at high temperatures (WHO, 2013; Castle Chemicals). In the southwest, it is important to note that water temperatures, especially during summer months, will be lower than air temperatures. A good rule of thumb is that for every 18°F (10° C) increase in temperature, sodium hypochlorite will degrade 3.5 times faster (Powell, 2019). In addition, sunlight can also increase the rate of chlorine decomposition (EPA, 1999).

As mentioned above, **pH** is also important because of how it impacts the distribution of free chlorine between HOCl and OCl-. At a pH of 6.5, approximately 95% of the free chlorine is in the more effective form of HOCl, while



Figure 4. Factors that influence chlorine efficacy.

only 5% is in the form of OCI<sup>-</sup>. Therefore, the target pH for ideal disinfection is between 6.0 and 7.5. (USDA NRCS; Zheng et al., 2008). If irrigation water reaches a pH of 7.5 or higher, it may require pH adjustment through acid addition to increase the efficacy of chlorine disinfection (Schwankl et al., 2012; USDA NRCS). It is important to remember that acids should never be added at the same injection point as chlorine in the distribution system, should not be stored with or next to chlorine, and should not be mixed with chlorine directly. If chlorine and acid are mixed directly, chlorine gas is likely to form, creating a hazardous situation for workers (ThermoFisher, 2018). Additional safety concerns are highlighted in **Figure 5**.

**Turbidity** is another factor that can impact the efficacy of chlorine disinfection. Turbidity, or the cloudiness of a water source, is a measure of how much light is scattered by suspended particles (USGS, 2016). These suspended particles are capable of creating excess chlorine demand and/or shielding pathogens from disinfection. The higher the turbidity reading, the higher the chlorine demand of the water will likely be, which increases the amount of chlorine required to inactivate microorganisms. Therefore, chlorine disinfection may be less effective in waters with higher turbidity. If there is a spike in turbidity before a planned irrigation or water sampling event, there are

## **Safety Considerations**

- Never inject acids and chlorine together as toxic gas may form
- Never store chlorine next to acids, oil, grease, fuel or other flammable materials
- Always add chlorine to water NEVER water to chlorine
- Always wear PPE:
  - ° Face shield/goggles
  - ° Long sleeves & gloves
  - ° Boots with socks

#### Figure 5. Safety issues of concern when using chlorine. Sources: Schwankl et al., 2012; USDA NRCS; EPA, 2014.

several options to ensure that chlorine disinfection is still effective: (1) increasing the chlorine dose; (2) increasing the contact time (if possible); or (3) waiting for sediments to settle. Any changes in water treatment should be coupled with verification of effectiveness with a microbiological test of the irrigation water post-treatment. It is also important to note that because temperature, pH, and chlorine residual and efficacy are interdependent and can change rapidly, these parameters should be measured on-site and in close proximity to the time and place of chlorine treatment.

**Microbial characteristics** include sensitivity or resistance to chemical treatments or the ability of an organism or biofilm to remain attached to a surface. These characteristics can vary greatly between individual organisms as well as aggregates, such as biofilms. If an organism is more resistant to chlorine, it will take longer to disinfect, and the chlorine will have to maintain contact for a longer amount of time. For example, the thick outer shell of a *Cryptosporidium* oocyst makes it almost entirely resistant to chlorine disinfection.

**Fertilizers,** specifically ammonium-containing solutions such as ammonium sulfate  $[(NH_4)_2SO_4]$  or ammonium nitrate  $(NH_4NO_3)$ , can also have an adverse effect on free chlorine residual. This is because free chlorine reacts with ammonia to form **chloramines**, which are less effective for disinfection. When ammonia is present in an irrigation water, mostly monochloramine  $(NH_2Cl)$  will form for Cl:N mass ratio up to 5:1. At Cl:N mass ratios greater than 7:1, breakpoint chlorination is achieved, and all chlorine added contributes to free chlorine residual (**Figure 3**). Because of these reactions, DO NOT apply chlorine at the same time fertilizers, herbicides, or insecticides are being injected (EPA, 2014).

Depending on your water source, **oxidizable substances** such as iron, manganese, and hydrogen sulfide can be found in varying concentrations. These substances react with chlorine to form insoluble compounds that can precipitate and potentially clog irrigation emitters and may need to be removed over time (USDA NRCS).

# What chlorine rates and methods for application should be used?

Control and inactivation of microorganisms can typically be maintained with free chlorine residual concentrations between 1 and 2 ppm when the pH of the water is between 6.0 and 7.5. To account for chlorine demand, an initial dose of between 5 and 6 ppm is typically sufficient to achieve this free chlorine residual at the farthest point from injection (e.g., at the last sprinkler head) (USDA NRCS). However, if the pH of the irrigation water is above 7.5 and acid addition is not possible, targeting a free chlorine residual of 2 ppm at the farthest point in the system may be sufficient (USDA NRCS). The USDA's Natural Resource Conservation Service (NRCS) suggests the following calculation to determine the amount of sodium hypochlorite to inject:

$$IR = Q \times C \times 0.006 \div S \qquad (Eq. 1)$$

Where:

**IR:** Chlorine Injection Rate (gal/hr)

- **Q:** System flow rate (gpm or gallons per minute)
- **C:** Desired applied chlorine concentration (ppm or parts per million)
- S: Strength of chlorine (% not fraction)

Example for 5.25% sodium hypochlorite:

Chlorine Injection rate =  $500 \text{ gpm x } 5 \text{ ppm x } 0.006 \div 5.25 = 2.85 \text{ gal/hr of chlorine}$ 

There are three common treatment scenarios for chlorination, and the applicability of each method depends on site-specific and water quality factors.

- Continuous treatment with 1-2 ppm of free chlorine residual is highly recommended for irrigation waters with higher biological loads and to prevent biological growth throughout the system.
- (2) Intermittent treatment with 5-20 ppm of free chlorine residual may be appropriate for systems experiencing a water quality upset (e.g., a spike in turbidity) or to eliminate biological buildup at the end of the growing season.
- (3) Shock treatment, or super chlorination, with >50 ppm of free chlorine residual may be performed annually or as a corrective measure for the irrigation system (USDA NRCS; Netafim, 2016).

It may be necessary, however, for continuous treatment when overhead irrigation is employed within 21 days of harvest for any crop that is overhead irrigated from an open irrigation water source, such as surface water, per Leafy Green Marketing Agreement (LGMA) metrics (AZ LGMA, 2020)

# Can chlorine be used in organic production of leafy greens or other raw agricultural commodities?

The use of chlorine in agricultural water used for irrigation is allowed under the USDA's National Organic Program (NOP) as long as the free chlorine residual does not exceed the U.S. EPA's maximum contaminant level (MCL) for drinking water of 4 ppm (USDA NOP, 2011). The NOP states that chlorine is "Allowed for disinfecting and sanitizing food contact surfaces. Residual chlorine levels for wash water in direct crop or food contact and in flush water from cleaning irrigation systems that is applied to crops or fields cannot exceed the maximum residual disinfectant limit under the Safe Drinking Water Act (currently 4mg/L expressed as Cl2)."

# How do you test irrigation water for chlorine residual?

Testing for free and total chlorine can be easy and inexpensive, and tests are widely available at local pool supply stores or through online vendors. These tests typically rely on a color change to determine the presence of chlorine, and the intensity of the color change indicates the concentration of chlorine. Because chlorine residuals can change rapidly as a function of environmental conditions and water quality, it is advisable to perform these tests frequently and at multiple points within the irrigation system. For example, tests performed near the injection point can aid in verifying the applied chlorine dose and instantaneous chlorine demand, and tests performed at the farthest point in the system can help determine if adequate disinfection has been achieved (e.g., free chlorine residual of 1-2 ppm) (USDA NRCS). **Table 4** shows examples and approximated costs of three chlorine testing methods described below.

One type of chlorine testing method involves test strips that are dipped in the water source for a specific amount of time (usually 5-15 seconds). The strip changes color depending on the chlorine concentration and can be compared to a color chart on the side of the bottle. Similarly, a color wheel test kit uses a powder or tablet of N, N-diethyl-p-phenylenediamine (DPD) that when added to a sample will cause it to turn pink in the presence of chlorine. In the presence of DPD and chlorine, the intensity of the color change is directly proportional to the amount of chlorine in the sample: the darker the pink, the higher concentration of chlorine. The sample is then compared to a color wheel to visually determine the concentration of chlorine. These two methods are the least expensive and easiest to use. However, drawbacks include method sensitivity, detection limits, user error, and a lack of calibration and standardization.

Table 4. Examples of me	ethods used to test	levels of chlorine.
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Testing Methods, Approximate Cost, &		Advantage	Disadvantage	
	Examples			
Test strips (\$10-\$15)	Image credit: Jessica Dery, UA	<ul> <li>Easy to use</li> <li>Inexpensive</li> <li>No equipment needed</li> <li>Measures free and total chlorine</li> </ul>	<ul> <li>User bias to match colors</li> <li>Approximation only (Qualitative)</li> <li>Interferences in water may skew result</li> </ul>	
Titration & Color Disc Kits (\$60 -\$150)		<ul> <li>Inexpensive</li> <li>Does not require a color match</li> <li>Readings based on permanent change in color</li> <li>Quantitative</li> </ul>	<ul><li>Lengthier process</li><li>Interferences in water may skew result</li></ul>	
Meters (\$300 and up)	Image credit: Jay Sughroue, BioSafe Systems	<ul> <li>Easy to use</li> <li>Eliminates user bias</li> <li>Quantitative</li> <li>Ability to test a multitude of water quality and chemical parameters using specific test strips or sensors</li> <li>Ability to store data</li> <li>Battery powered for use in field</li> <li>Measures free and total chlorine</li> </ul>	<ul> <li>Higher initial investment</li> <li>May be sensitive to light and temperature</li> </ul>	

\*Estimated costs per method type are provided. The University of Arizona shows examples of products but does not endorse any specific manufacturer. Below are links to select products.

A similar DPD-based method uses a **calibrated digital colorimeter** to measure the color change and automatically report the chlorine concentration in ppm. While this method is fast and accurate, the cost of the colorimeter is greater than the test strips and color wheel approach mentioned above. These methods also allow for differentiation of total chlorine residual (i.e., color change after specified reaction time) and free chlorine residual (i.e., immediate color change). Then the difference in the measurements can be used to estimate the combined chlorine concentration (i.e., total chlorine residual – free chlorine residual).

## What about plant sensitivities?

Plant growth, appearance, and health may also be impacted by the use of chlorine in irrigation water. If chlorine is used in excess, the chance of phytotoxicity is increased. Phytotoxicity is an injury to a plant when exposed to chemicals or other toxins that can affect

physiological processes such as growth, germination and yield. Sensitivity levels vary between crops, so understanding what appropriate levels should be for a specific crop type should be understood before selecting an appropriate chlorine dose for treatment. Some plants with known sensitivities include starch potatoes, tomatoes, peppers, strawberries, cucumbers, lettuce, and melons (K+S Minerals and Agriculture GmbH, 2019). Symptoms include a bleaching appearance to the tissues (chlorosis), dark spots on the surface of the leaves (necrotic mottling) or other discolorations, leaf curl, decreased plant growth, and cell and tissue death (foliar necrosis), among others (Zhang et al., 2008). Chlorine toxicity thresholds for select agricultural commodities can be seen in Table 5. For example, free chlorine concentrations between 15 and 25 ppm were effective at pathogen control with minimal phytotoxicity in sweet pepper plants, but serious toxicity was observed at concentrations greater than 50 ppm (Ehret et al., 2001).

Table 5. Free chlorine phytotoxicity threshold estimates for selected agricultural commodities.

Commodity	Chlorine threshold (ppm)
Vegetable seedlings	<1
Peppers	>8
Tomatoes	>8
Sweet peppers	>50
Broccoli	>37
Source: Zheng et al., 2008.	·



Figure 6. Benefits and drawbacks of using chlorine as a treatment option for agricultural irrigation water.

#### Summary

Chlorine has been used for decades as an effective and affordable way to disinfect water, from drinking water to agricultural irrigation water. Unlike other treatment methods (e.g., ultraviolet light and ozone), chlorination has been historically used by the drinking water industry to impart residual disinfection within the distribution system. It is a cost-effective and reliable method to reduce a variety of pathogens that are of concern in food safety, meet new water quality standards, and protect public health. It is important to remember that fertilizers and pesticides should not be used at the same time as chlorination and that turbidity may reduce disinfection efficacy. In addition, make sure to always measure the amount of *free chlorine* and not the total chlorine, as the free chlorine is what is available for disinfection. Figure 6 summarizes some benefits and drawbacks to using chlorine as a method of treatment for agricultural irrigation water.

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## Endnotes

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