THE UNIVERSITY OF ARIZONA
Cooperative Extension

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Minimizing Risks: Use of Surface Water in Pre-Harvest Agricultural Irrigation; Part III: Peroxyacetic Acid (PAA) Treatment Methods

Jessica L. Dery, Vijay Choppakatla, Jay Sughroue, and Channah Rock

What is Peroxyacetic Acid?

Peroxyacetic acid (also known as peracetic acid or PAA) is a colorless liquid with a low pH and a strong, pungent, vinegar-like odor. PAA is commonly used as an antimicrobial agent for both non-porous hard surfaces and water in various industries, including agriculture, food processing, beverage, wastewater, hospitals, health care, and pharmaceutical facilities. It is approved by the US Environmental Protection Agency (USEPA) for use in agricultural waters as a crop protection tool and is allowed under the National Organic Program (NOP) for the production of organic crops, livestock, and food handling (USEPA, 2012; NOP, 2016; USDA 2016). In Europe and the US, it has been used for many years in wastewater treatment plants (WWTP) as an alternative to chlorinated compounds, due to concerns of the creation of potentially harmful disinfection by-products (DBPs) when chlorine-based compounds come into contact with organic matter (USEPA, 2012). More recently, PAA is quickly gaining interest as a treatment option for agricultural irrigation water to reduce potential pathogens, protect public health, meet new food safety guidelines, and reduce the environmental impact on soils and crops (Nguyen et al., 2014).

PAA is a strong oxidant and fast acting disinfectant with biocidal and viricidal properties (Kitis, 2004; USEPA, 2012). Commercially available solutions of PAA are a combination of aqueous mixtures of peroxyacetic acid, acetic acid, hydrogen peroxide, and water at various concentrations with an added stabilizer to slow decomposition (**Figure 1**) (Profaizer et al., 1997; Nguyen et al., 2014; USDA, 2016). While hydrogen peroxide is also a disinfectant, PAA is a more active and potent antimicrobial agent (Profaizer et al., 1997; Kitis et al., 2004).

Key Points

- PAA is an excellent bactericide and effective against a variety of microorganisms
  - Effective across a wide range of temperatures and pH values encountered in irrigation waters
  - Typically used in concentrations of 5 to 10 parts per million (ppm) for irrigation water treatment
  - Commonly used for post-harvest wash water applications and hard surface disinfection to control human health pathogens and spoilage organisms

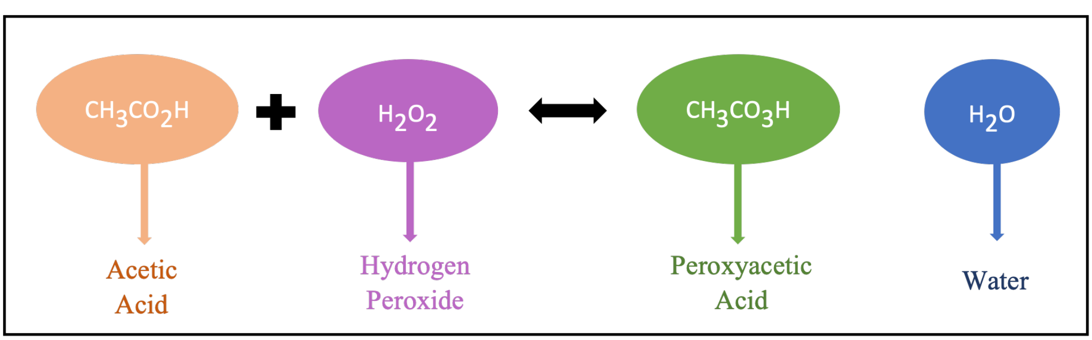

Figure 1. Chemical makeup of peroxyacetic acid (PAA).

- Is an effective crop protection tool to control both bacterial and fungal plant pathogens
- PAA does not leave behind toxic DBPs: breaks down into oxygen, carbon dioxide and water
- When using PAA, make sure to follow directions according to the label
  - Personal protective equipment (PPEs) should always be used when handling PAA concentrate as it can cause eye and respiratory problems

What does PAA treat?

PAA is used to treat pathogenic, or disease-causing microorganisms found in water that concern the fresh produce industry. While disinfection with PAA is effective across a wide range of microorganisms that pose food safety and health risks, some microorganisms are more resistant to PAA than others (Lazarova et al., 1998; Liberti et al., 1999; Kitis, 2003). Mainly used in the food industry, PAA has been utilized since the 1950's to reduce spoilage of fruits and vegetables by removing microorganisms and fungi. It is currently used as a disinfectant in irrigation water and produce wash water, as a sanitizer for surfaces that come into contact with produce, and to remove deposits and prevent biofilm formation on food contact surfaces (Lenntech, 2020; Pfuntner, 2011; USDA, 2016). A general ranking of PAA effectiveness on various microorganisms, from most effective to least effective is: bacteria > viruses > bacterial spores > and protozoan cysts (**Table 1**) (Kitis, 2004). PAA is least effective at inactivating some parasites such as *Giardia lamblia* cysts and *Cryptosporidium parvum* oocysts as well as some viruses (Kitis, 2003; Lazarova et al., 1998; Lefevre et al., 1992; Liberti et al., 1999).

What happens when PAA is added to irrigation water?

As PAA is added to water, there is a release of active oxygen, which is responsible for the oxidation process and disinfecting properties. Most disinfection occurs within the first ten or fifteen minutes of contact time (Kitis, 2003; Nguyen et al., 2014). As PAA degrades, it breaks down into its original components: hydrogen peroxide and acetic acid, which further break down into water, oxygen, and carbon dioxide. When PAA breaks down, it does not persist or leave behind any residual DBPs, making it an environmentally friendly treatment option (Nguyen et al., 2014; USDA, 2016; Lenntech, 2020).

Table 1. Log reductions of select pathogens-of-concern to the fresh produce industry from WWTP effluent and surface waters used for agricultural irrigation.

Organism	Water Source	PAA (ppm)	Contact Time (min)	Log Reduction	Source
			Bacteria		
Clostridium Perfringens spores	WWTP Effluent	2.0 - 4.5	20-30	<1 (97.4 – 99.7%)	Briancesco et al., 2005
E. coli; Total Coliform Bacteria	WWTP Effluent	1.5 - 2.0	20	5	Stampi et al. 2001
E. coli (TVS 353)	Surface [a]	12.7	5	>3.71	Rock et al., unpublished data 2020
E. coli (TVS 353)	Surface [b]	6	-	>4.99	Rock et al., unpublished data 2020
E. coli	Surface [c]	4, 6	15, 5	6	LaBorde, 2014
E. coli	Surface [d]	2.5	1.3	3.20	Chang, 2015
Fecal Coliform Bacteria	WWTP Effluent	2.0 - 2.5 (residual = 0.8)	15	2.7	Nguyen et al., 2014
Salmonella enteritidis	WWTP Effluent	1.5 - 3	10	2 -3	Koivunen et al., 2005
			Parasites		
Cryptosporidium oocysts	WWTP Effluent	2.0 - 4.5	20 - 30	<1 (71 – 75%)	Briancesco et al., 2005
Giardia cysts	WWTP Effluent	2.0 - 4.5	20 - 30	<1 (91.6 – 96.5%)	Briancesco et al., 2005
			Viruses		
Hepatitis A	Produce Wash Water	100	2	0.7	Fraisse et al., 2011
Norovirus	Produce Wash Water	100	2	2.3	Fraisse et al., 2011

[a]Bench-top trial using Colorado River Water (CRW) used for agricultural irrigation at the Maricopa Agricultural Center in Maricopa, AZ; [b]Full-scale field trial in a continuous flow irrigation system using CRW at the Maricopa Agricultural Center in Maricopa, AZ; [c]Bench-top trial using pond water from Russell E. Larson Agricultural Research Center, Rock Springs, PA; [d] Full-scale field trial in a continuous flow irrigation system using pond water from the Plateau AgResearch and Education Center, Crossville, TN.

How are pathogens controlled using PAA?

PAA mechanism for disinfection is through the direct oxidization, or the loss of electrons, of the cell wall of microorganisms. When electrons are lost from the cell wall, bonds between enzymes and proteins break apart, disrupting the cell structure. As the cell wall and cell membrane continue to break apart, cellular activities shut down, intracellular components leak out and are further destroyed, and ultimately, cell death occurs (USEPA, 2012; Nguyen et al., 2014). PAA is a stronger oxidizing agent than all forms of chlorine including sodium hypochlorite, calcium hypochlorite, and chlorine dioxide but weaker than ozone (Kunigk et al., 2001a; NOSB, 2000; USDA, 2016). **Table 2** shows the oxidation capacity of disinfectants commonly used in the agriculture industry based on electron volts (eV), a unit used to measure the potential energy of an electron. The higher the eV, the higher the oxidation potential, and the more effective the disinfectant.

What factors influence the effectiveness of PAA?

The effectiveness of PAA is influenced by several factors such as the quality of the source water, applied dose, contact time, and characteristics of the microbe (USEPA, 2012; Kitis, 2003). Water quality characteristics that may affect treatment efficacy include temperature, pH, total suspended solids (TSS), biological oxygen demand (BOD), and nephelometric turbidity units (NTU) (Kitis, 2003). TSS are any solids including salt, plant and animal matter, and waste products; BOD is the amount of oxygen that microorganisms consume as they decompose, or break down, organic matter; and NTU is a measure of the water's clarity, or how much it scatters light.

Parameters such as pH, organic matter content, and temperature may be less of an issue with PAA relative to other treatment chemistries. PAA is effective over a wide range of temperatures between 0°C/32°F to 40°C/104°F (Leaper, 1984; Taylor, 2017). Additionally, the pH of the irrigation water may also affect the efficacy of disinfection, but very minimally (Baldry et al.,1991; 2006; Nguyen et al., 2014). It has been found that at PAA works best under slightly acidic and neutral conditions where pH values are between 5 to 8. (Baldry et al., 1991; Bigliardi et al.; Kitis, 2003).

PAA has the advantage of being a potent disinfectant at low concentrations and short contact times (Profaizer et al., 1997; Kitis, 2004; USEPA, 2012; Nguyen et al., 2014). Previous studies in WWTPs were successful at reducing E. coli, Total Coliform bacteria, Fecal Coliform bacteria, and *Salmonella* concentrations by 2 to 5-logs. In these trials, PAA concentrations were between 0.8 to 3 ppm and contact times ranged from between 10 to 20 minutes (Stampi et al., 2001; Nguyen et al., 2014; and Koivunen et al., 2005).

Over the last ten years, PAA has been studied more intensely as an option for irrigation water treatment by both university and private researchers. Several variables have been studied to evaluate their relative importance on the effectiveness of PAA for killing human health pathogens or indicator organisms in irrigation water. The effective PAA concentrations varied between 1 and 20 ppm depending on the bacteria group and inoculum level, water source, and contact time (Laborde, 2014; Rock et al., unpublished data, 2020). Initial dose concentration and contact time are the two variables with the greatest influence on the effectiveness of PAA to treat irrigation water (Laborde, 2014; Rock et al., unpublished data, 2020).

A 2014 study conducted by Laborde (2014) evaluated PAA (SaniDate® 12.0, BioSafe Systems, East Hartford, CT) for *E. coli* control using surface water (pond water) collected from the Russell E. Larson Agricultural Research Center, Rock Springs, PA and inoculated with *E. coli* (non-pathogenic strain-K12). Five concentrations of PAA (2, 4, 6, 8, and 10 ppm) with different contact times (2, 5, 15, or 30 min) were evaluated. The results shown in **Figure 2** indicate that the rate of destruction of *E. coli* increases with increasing concentration of PAA. For the negative control (no sanitizer; not shown in figure) and the 2 ppm treatment, less than a 0.5-log CFU/g reduction of *E. coli* occurred after 30 min. At 4 and 6 ppm PAA, a 6-log reduction occurred after 15 and 5 min, respectively. However, at 8 and 10 ppm PAA, a 6-log reduction occurred after only 2 min.

Table 2. Oxidation capacity of selected sanitizers/disinfectants used for agricultural irrigation.

Sanitizer	eV*
Ozone	2.07
Peracetic Acid	1.81
Chlorine Dioxide	1.57
Sodium Hypochlorite (chlorine bleach)	1.36

* electron-Volts is a unit of energy. The higher the eV, the greater the oxidation capacity.
Source: NOSB, 2000.

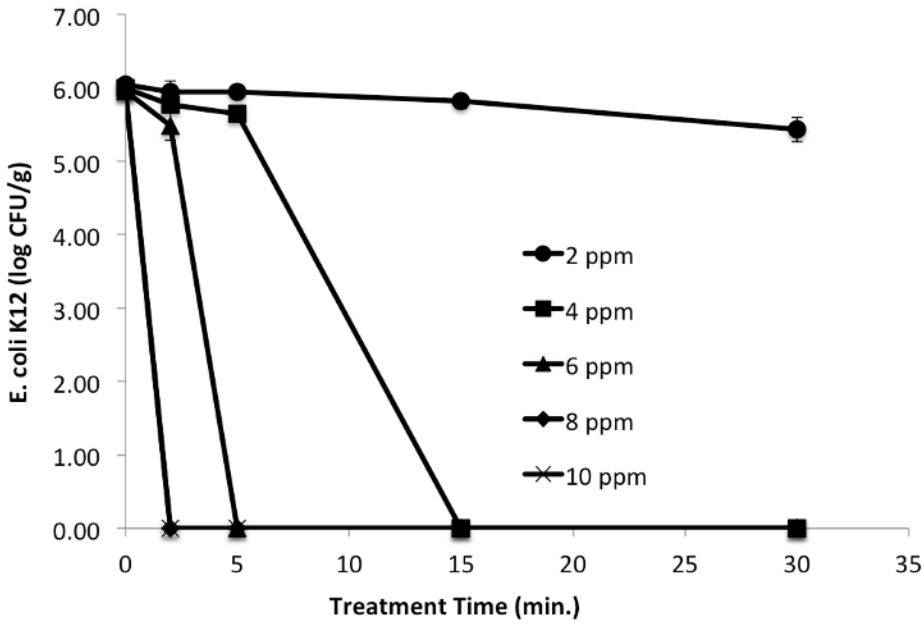

Figure 2. Effect of PAA concentration in SaniDate® 12.0 on the destruction of E. coli. (*8 and 10 ppm lines are overlapping. Each data point is the mean of three replicate experiments*)

More recently, research trials conducted by the University of Arizona in 2019 investigated the effectiveness of various PAA formulations. Both benchtop and full-scale field trials, using surface water (Colorado River Water, CRW) for agricultural irrigation, found that PAA concentrations between 5-20 ppm were very effective in reducing generic *E. coli* and Total Coliform bacteria below detectable levels. The benchtop study showed a >3.71 log reduction of generic *E. coli* using 12.7 ppm at 5 minutes contact time (Rock et al., unpublished data, 2020). The full-scale field trial showed generic *E. coli* log reductions of >4.99 with 6 ppm PAA in a continuous flow irrigation system at both the middle and last sprinkler heads. **Table 1** provides a summary of microbial log reductions in both WWTP effluent as well as surface waters used for agricultural irrigation water based on organism, dosing concentrations, and contact times.

Microbial characteristics also play an important role in the disinfection efficacy of PAA. While studies on the inactivation of human pathogenic viruses in irrigation water are limited, studies on PAA efficacy against some viruses relevant to produce safety have been performed on produce wash water. These show that viruses may be more resistant to chemical disinfection, including PAA, than bacteria. Fraisse et al. found that using 100 ppm of PAA for 2 minutes resulted in log reductions of 0.7 for Hepatitis A and 2.3 for Norovirus, both of which are of food safety concerns. Studies on WWTP effluents also support these findings: that viruses, as well as parasites (protozoans), may be more resistant to chemical disinfection. *Giardia* cysts and *Cryptosporidium* oocysts showed less than 1 log reduction at 2.0 to 4.5 ppm at 20 to 30 minutes of contact time (**Table 2**). It should be noted that other chemical disinfectants, such as sodium and calcium hypochlorite, are also less effective at reducing some viruses and parasites. While viruses and protozoans are not mandated to be tested under the Food Safety Modernization Act (FSMA) Produce Safety Rule (PSR) or the Leafy Green Marketing Agreement (LGMA) metrics, they are a food safety and public health concern.

What are the advantages of using PAA?

There are many advantages of treating irrigation water with PAA. It is approved by the USEPA, has a long shelf-life, is easy to use, is not considered to be mutagenic or carcinogenic, and is less corrosive to equipment than hypochlorites (Liberti et al., 1999; Nguyen et al., 2014; Pfuntner, 2011; Kitis, 2003). The costs are comparable to sodium and calcium hypochlorite and startup typically requires minimal capital investment; however, this depends on the dosing and concentration needs (Nguyen et al., 2014; USEPA, 2012; USDA, 2016). PAA will not contribute to increased sodium or chlorides in the soil profile, unlike chlorine-based chemistries, and there are no measurable effects on pH or BOD. As PAA breaks down it leaves behind no residual disinfection by-products, making it an environmentally friendly treatment option. Low concentrations are effective across a wide range of microorganisms and in the presence of organic matter, protein residues, or nitrogen fertilizers (Nguyen et al., 2014; Kunigk et al., 2001b; USDA, 2016), helping to keep production costs down while meeting new regulatory demands and protecting public health. The risk of phytotoxicity is negligible when treating irrigation water with PAA and the EPA has approved PAA as a fungicide/bactericide used to spray crops at rates 20-30 times stronger than used for irrigation water treatment.

What are the disadvantages of using PAA?

Historically, treating irrigation water with PAA cost slightly more than using sodium hypochlorite but new higher concentrations approved by the EPA for irrigation water treatment are available which significantly reduce the cost. Another potential disadvantage is that transporting large quantities of PAA require hazmat drivers. All workers coming into contact with the concentrated and undiluted PAA must be trained as pesticide handlers and must wear the proper PPE as the concentrated solution can cause irritation to the skin, eyes, and respiratory system (CDC, 2017). A side-by-side comparison of benefits and drawbacks of using PAA as an irrigation water treatment can be seen in **Figure 3**.

What are recommended PAA rates and methods for application?

PAA can be applied through any type of sprinkler irrigation system (solid set, center pivot, traveling gun) or drip/micro sprinkles. PAA is commonly drawn directly from the source container (drums/totes) and injected into the irrigation system via either metering pumps (positive displacement) or venturi type injectors. Metering pumps, which are controlled by a flow meter, are the most precise method for chemigating PAA. For vegetable production in Arizona and California, research and grower data has shown that injection rates of between 5-10 ppm are optimal for meeting various food safety requirements by associations, FMSA, or customers.

How do you test irrigation water for PAA during irrigation water treatment?

Testing PAA in irrigation water can be easy and inexpensive, and tests are readily available for purchase through multiple online suppliers. These include methods that rely on a color change to approximate levels of PAA (qualitative assessment), whereas other (quantitative) methods require the use of a meter and provide more accurate measurements. PAA is often measured in ppm, which is equivalent to mg/L. Most methods, depending on the manufacturer and specific product, are able to measure a wide range of PAA concentrations used in agricultural settings. Testing at the first sprinkler head, nearest the injection site, will verify the applied dose, while testing at furthest sprinkler head from the injection point will help to determine that sufficient treatment and disinfection is achieved throughout the system. A side-by-side comparison of available testing methods used for testing PAA in agricultural irrigation waters can be seen in **Table 3.**

Simple colorimetric test strips are the easiest and least expensive option used for the estimation of PAA in a water sample. The user collects a water sample, dips the test strip in, and compares the color change on the strip to a standard on the product label. Because the reading is based on a color match, the estimation of PAA concentrations may vary by user. Testing strips used on a daily basis are relatively inexpensive.

Titration kits are another option, although they are more time consuming and may involve a relatively simple calculation to quantitatively determine concentration.

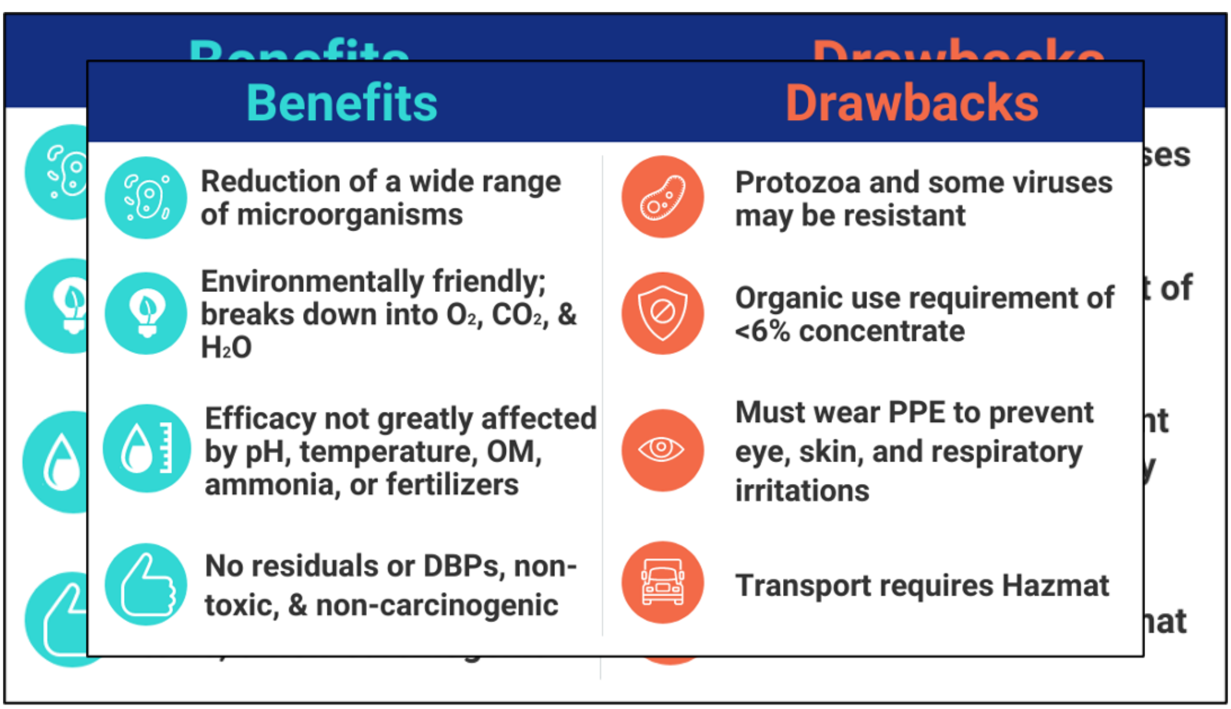

Figure 3. Benefits and drawbacks of PAA as an irrigation water treatment method.

Table 3. Comparison of testing methods for measuring PAA in irrigation water samples.

Test strips ($10-$15)	  *Image credit: LaMotte PAA test strips (left) & Jay Sughroue with Quantofix PAA strips (right).*	▪ Easy to use ▪ Inexpensive ▪ No equipment needed	▪ User bias to match colors ▪ Qualitative- approximation only ▪ Not suitable for low PAA applications
Titration ($60-$120)	 *Image credit: Jay Sughroue, BioSafe Systems*	▪ Inexpensive ▪ Does not require a color match. ▪ Readings based on permanent change in color ▪ Quantitative	▪ Lengthier process ▪ Involves calculations ▪ May not measure below 5 ppm
Meters ($300-$700)	 *Image credit: Jessica Dery, University of Arizona*	▪ Easy to use ▪ Eliminates user bias ▪ Quantitative ▪ Ability to test a multitude of water quality and chemical parameters using specific test strips or sensors ▪ Ability to store data ▪ Battery powered for use in field	▪ Higher initial investment ▪ May be sensitive to light and temperature ▪ May not measure levels of PAA below 5 ppm

However, the advantage is that the reading is based on a permanent color change, from dark blue to clear, which can eliminate user bias.

Meters are another option for quantitatively measuring PAA in water samples. They are easy to use, portable, and are able to measure and store various water quality and chemical parameters, depending on the meter. They eliminate user error, but some meters may be sensitive to light and temperature. They may require a larger capital investment than qualitative methods.

PAA probes used in other industries, including post-harvest fruit and vegetable wash water applications, are now being used to continuously monitor and record PAA residual levels for irrigation water treatment. Cloud based monitoring and recording provides growers and food safety managers increased real-time accessibility to ensure that target parameters are being met. The cost associated with implementing this new technology is offset by the ability to meet the ever-increasing food safety requirements.

What about plant sensitivities?

PAA is commonly used in both greenhouse settings and produce processing plants, and there is evidence of minimal impact on plant tissue or crop quality. In a field study conducted at Penn State University strawberry blossoms submerged in PAA solutions (SaniDate® 12.0) up to 18 hours exhibited no damage to blossoms or fruit development (LaBorde, 2014). Alternatively, studies on hydroponically grown produce have shown conflicting results. Tomato root systems exposed to PAA demonstrated a decrease in oxygen uptake, but shoots showed no negative effects (Vines et al., 2003), whereas exposure of hydroponically grown water cress to PAA resulted in increased oxygen uptake, growth, and yield (Carrasco et al. 2011). Note that because hydroponically grown produce lack soils, which can buffer chemical treatments and reduce root stress, these studies do not adequately mimic *in-field* applications. In general, *in-field* water treatment applications, when managed appropriately, have demonstrated minimal impact on crop health or quality.

In summary

Peroxyacetic acid has been used for decades as a high-level disinfectant/sanitizer in industries that require aseptic environments. Specifically, PAA is used in agricultural post-harvest applications as an antimicrobial agent to control human health pathogens and spoilage organisms in wash water (hydrocoolers, flumes, vats and spray bars) and on non-porous hard surfaces. More recently, it is becoming an environmentally friendly treatment alternative for irrigation water treatment as it does not leave behind toxic DBPs and is safe for all crops. Additionally, it is effective against a variety of microorganisms that are of concern for food safety over a wide range of water temperatures and pH values. It is cost effective, easy to use, and its disinfection efficacy is not significantly influenced by the presence of organic matter, ammonia, or organic nitrogen fertilizers. University studies have demonstrated it as an effective treatment option for agricultural irrigation water to help meet new water quality standards and protect public health.

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THE UNIVERSITY OF ARIZONA
Cooperative Extension

AUTHORS

Jessica L. Dery
Assistant in Extension, Water Quality and Food Safety, Maricopa Agricultural Center

Vijay Choppakatla, Ph.D.
Plant Pathologist, BioSafe Systems

Jay Sughroue, Ph.D.
Regional Manager, BioSafe Systems

Channah Rock
Water Quality Specialist & Professor
University of Arizona, Maricopa, AZ

CONTACT
Channah Rock
channah@cals.arizona.edu

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