Chlorate Residues as a Potential Trade Barrier to the EU

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Min-Jeong Suh, Ph.D. and Adam Simpson, Ph.D.

The Hall Lab at USDA-ARS
San Joaquin Valley Ag. Science Center

1. Fast Response to Industry / Scientific Residue Issues
    a. Emerging Toxins / Contaminants
        i. Mineral Oil (Mosh / MOAH)
        ii. Tenuazonic Acid
    b. Smoke Exposure and other Quality Markers
2. Pesticide Residue Analysis for Regulatory Purposes
3. Agrochemical Residue Method Simplification and Publication
4. Harm Reduction for Agrochemical Use

The Hall Lab at USDA-ARS
San Joaquin Valley Ag. Science Center

1. Fast Response to Industry / Scientific Residue Issues
2. Residue Analysis for Regulatory Purposes
   a) New Registration and Registration Renewals for Post-Harvest Fumigants
3. Agrochemical Residue Method Simplification and Publication
4. Harm Reduction for Agrochemical Use

The Hall Lab at USDA-ARS
San Joaquin Valley Ag. Science Center

1. Fast Response to Industry / Scientific Residue Issues
2. Residue Analysis for Regulatory Purposes
3. Agrochemical Residue Method Simplification and Publication
    a) Reducing the Cost of Residue Testing
    b) New Technologies
    c) Education and Mentorship
    d) Public / Industry Outreach
4. Harm Reduction for Agrochemical Use

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1. Fast Response to Industry / Scientific Residue Issues
2. Residue Analysis for Regulatory Purposes
3. Agrochemical Residue Method Simplification and Publication
4. Harm Reduction for Agrochemical Use
   a. Fate and Transport
   b. Unexpected Interactions and Metabolites
   c. Public / Worker Exposure

Chlorate Residues as a Potential Trade Barrier

- Background / Introduction
- Chlorate Residues in Prunes
- Lab Work
- Thoughts / Recommendations

Introduction

- In the 2018 Annual EU Pesticide Report
  - Chlorates one of the most common residues found and the most likely to be violative (~10%)
  - The residue most often found in baby food
  - The residue most often found in organic food
  - 2019 results essentially the same
- New Chlorate MRLs for the EU were ratified in 2020:
  - 0.05 ppm for small berries and stone fruit (prunes)
  - 0.1 ppm for tree nuts
  - 0.3 ppm for figs and dates
- If this leads to increased surveillance, chlorate is a potential trade barrier

Introduction

- (Sodium) Chlorate is no longer directly applied as a pesticide, instead it forms as a sanitation by product
- Most dietary exposure comes from drinking water
  - ~ 80% of the "risk cup"
- Potential sources for chlorate residues in food include the use of hypochlorite (bleach), chlorine dioxide, and chloramines

Chlorate Residues and FSMA

Choosing an Antimicrobial Product, Including Sanitizers

- Chlorine sanitizers are commonly used
  - Affordable and available
  - Corrosive, highly reactive
- Many non-chlorine chemical options
  - Ozone, peroxyacetic acid, hydrogen peroxide, etc.
- Organic formulations are available
  - Tsunami, Spectrum, Sanidate, VigorOx 15 F&V, etc.
  - Check with organic certifier
- Must be labeled for use on produce

Produce Safety ALLIANCE

Monitoring pH

- Water pH can affect the efficacy of sanitizers, especially chlorine
- There are many ways to monitor pH
  - e.g., pH test strips, handheld pH meters, and titration kits
- Adding chlorine and other sanitizers may change the pH of water
  - You must monitor treatment
  - You should adjust pH as needed based on the optimal pH range for effective use of your sanitizer

§

Produce Safety ALLIANCE

The Project

A two year TASC Grant (2020-10) with the goal of preserving trade by:

1. Collect Data on the Typical Levels of Chlorate in US Dried Fruit and Tree Nuts
2. Identify the Sources (Pre- and Post-Harvest) of Chlorate Residues
3. Issue Recommendations on Reducing Chlorate Residues

Collaborators

1. Spencer Walse – Post-Harvest Chemist, USDA-ARS
2. Bill Mitch – Environmental Engineer, Stanford University

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Chlorate Testing Results

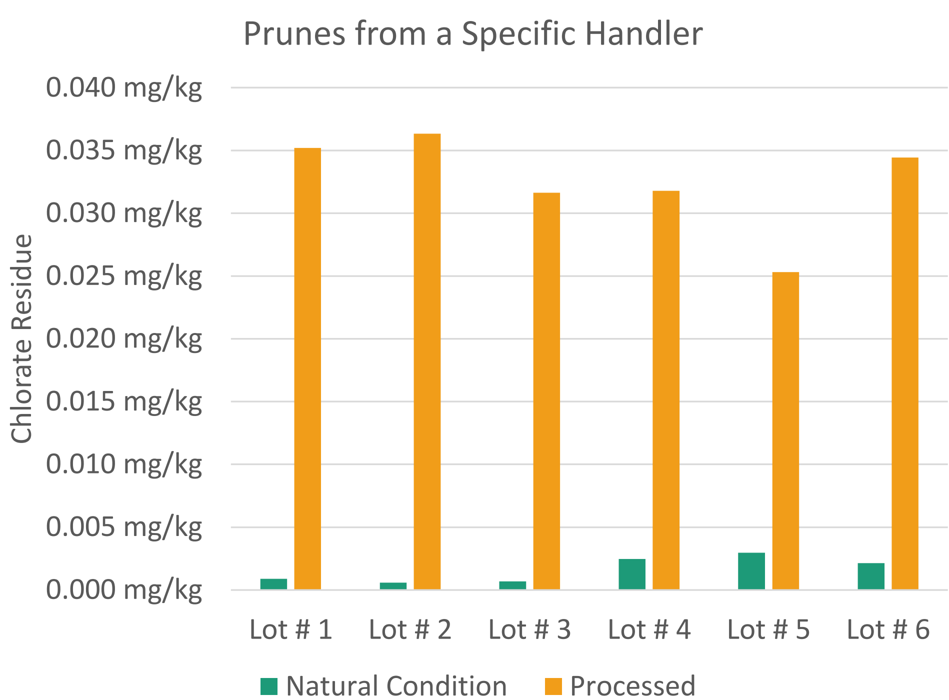
Results from SFA Survey Testing

Reportable residues			Violative Residues	
Commod.	#	%	#	%
Prune – 2020	17 / 23	74%	7	30%
Prune – 2021 and 2022	38 / 59	64%	1	2%

The Drop May Be Due to Testing Mostly Low Moisture Product in 2021/2022

Chlorate Testing Results

Results from an Individual Facility



Overall Results for Prunes from 2020

Prune Results from 2020	
Avg Pre	0.003
Avg. Post	0.032

From the 2020 CY Results:

~ 0.03 (30 ppb, 60% of MRL) increase in Chlorate Residues was observed in processed vs non-processed Prunes

Chlorate Testing Results

Results from SFA 2020 / 2021 Testing				
Reportable residues			Violative Residues	
Commod.	#	%	#	%
Prune – 2020	17 / 23	74%	7	30%
Prune – 2021	24 / 46	52%	**1**	**2%**
Prune – 2021 (plus 30 ppb)			**8**	**17%**

Chlorate Testing Results

Overall Testing Results for 2021:

Table 1: Survey Results

	# Samples	# Residues	# Exceed[2]	Average[1]	Median[1]	Max[1]	Min[1]
Almond	38	4	0	> LOD	0.000	0.009	> LOD
Prune	59	38	1	0.011	0.008	0.073	> LOD
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
Bleached[3]	26	20	18	2.344	1.741	7.888	> LOD
Unbleached[3]	21	10	0	0.008	0.000	0.059	> LOD

Almonds (<u>Dry Processed</u>) had **by far** the Lowest Incidence of Chlorate Residues

(1) Non Detect and residues under the LOD of 0.005 mg / kg were treated as 0 residues for these calculations
(2) Compared to the EU MRL for stone fruit and small berries: 0.05 mg / kg for prunes and compared to the EU MRL for tree nuts: 0.100 mg / kg for almonds, pistachios and walnuts.
(3) The "Bleached" and "Unbleached" values are a subset of the total walnut numbers

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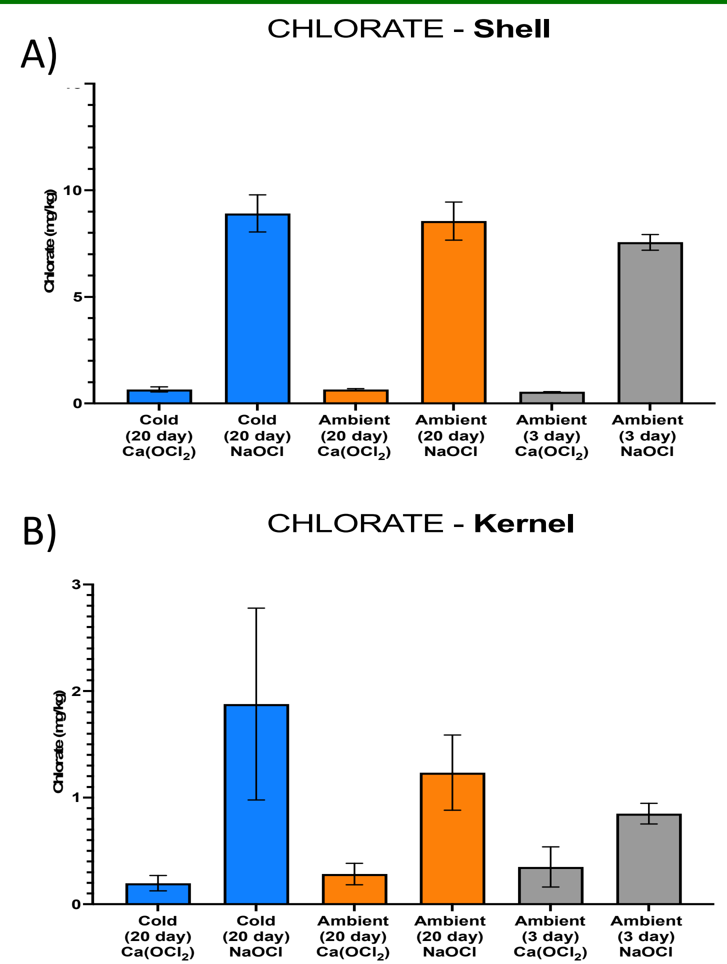
Key Findings from the Walse Lab

- Simulated Walnut Bleaching by Dr. Adam Simpson
- 2.75 min Residence @ 21°C
- NaOCl vs $Ca(OCl)_2$ (Standardized to 3.25% Free Chlorine) **– Largest Effect**
- Ambient (21°C) vs Cold (3 °C) Storage
- 3 Days Storage vs 20 Days

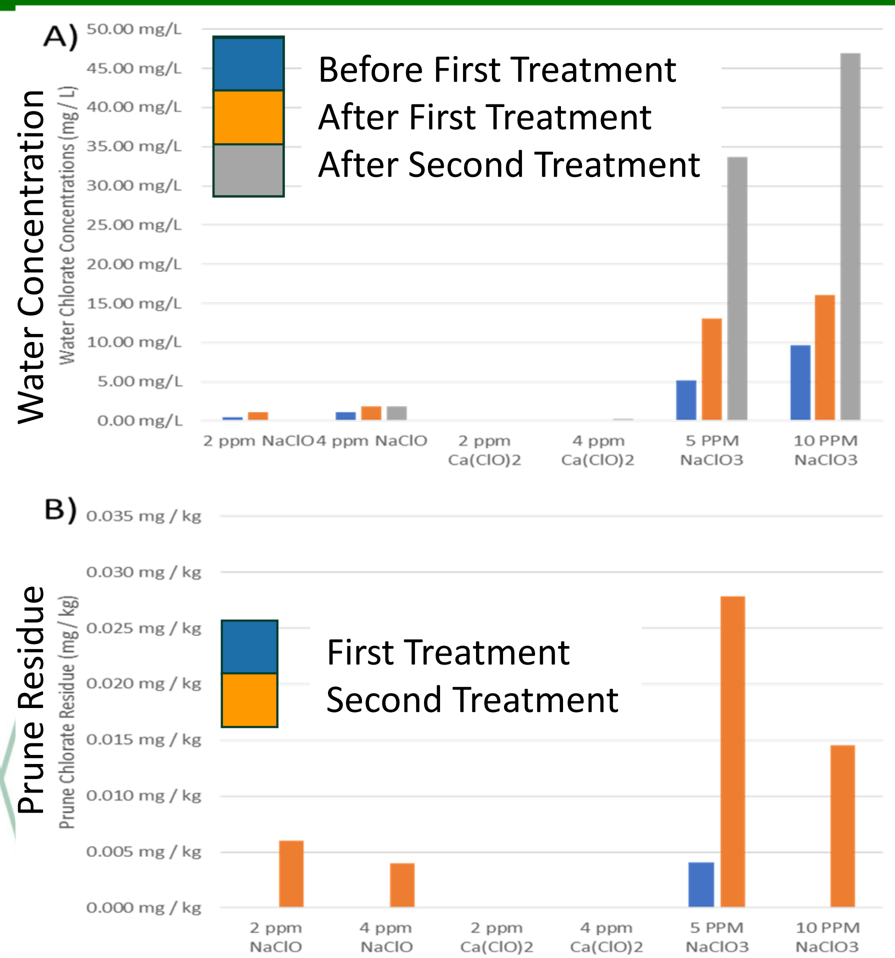


Key Findings from DFA of CA

- Little Increase in Chlorate Residues Associated with Steam Rehydration of Prunes

- Chlorate Does Build in the Rehydration Water Over Successive Treatments

- Higher Residues from NaClO Compared to $Ca(ClO)_2$

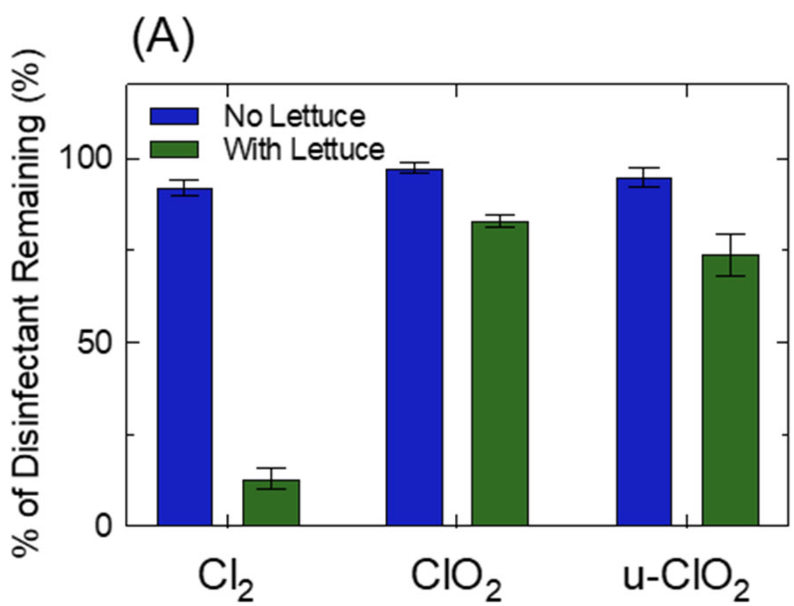


Key Findings from the Mitch Lab

Purified Chlorine Dioxide as an Alternative to Chlorine Disinfection to Minimize Chlorate Formation During Post-Harvest Produce Washing

Min-Jeong Suh[1] and William A. Mitch[1,]*
[1] Department of Civil and Environmental Engineering, Stanford University, 473 Via Ortega, Stanford, California 94305, United States

- Less Chlorine Dioxide Consumed by OM compared to Chlorine



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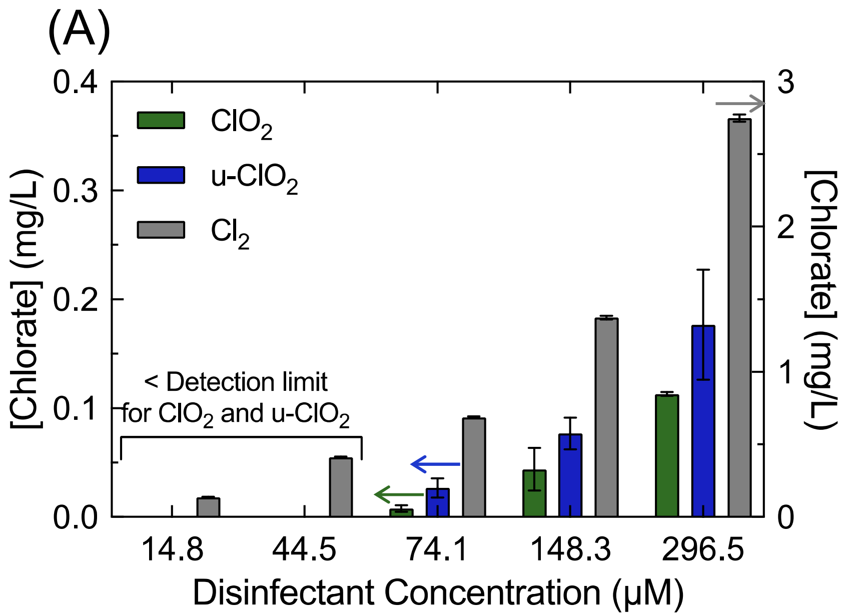
- Lower Levels of Chlorate formed by using Chlorine Dioxide



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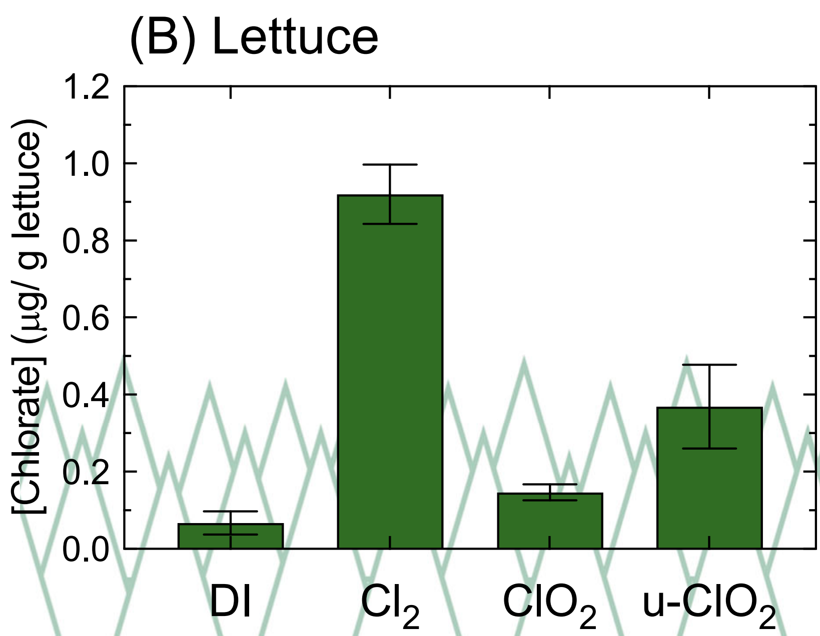
- Lower Levels of Chlorate formed by using Chlorine Dioxide
- Less Chlorate Found in Produce Washed with Chlorine Dioxide



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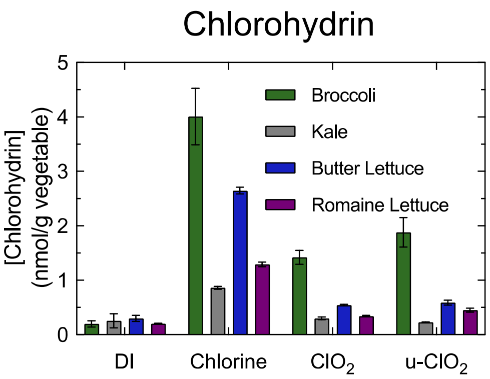
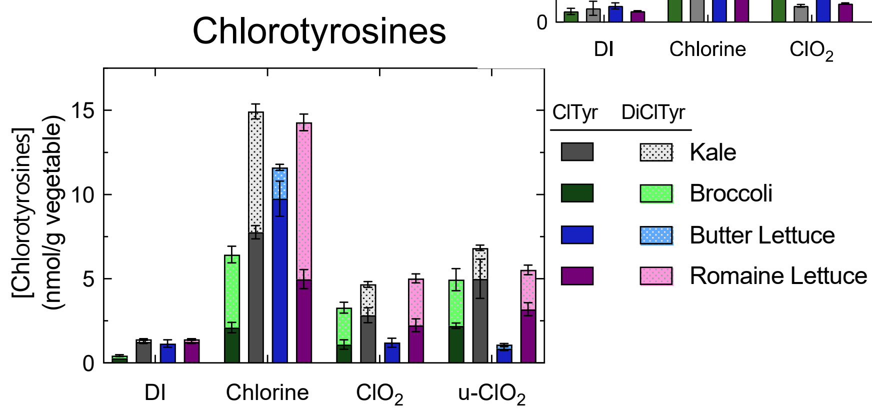
- Less Chlorine Dioxide Consumed by OM compared to Chlorine
- Lower Levels of Chlorate formed by using Chlorine Dioxide
- Less Chlorate Found in Produce Washed with Chlorine Dioxide
- Lower Amounts of Other DBPs as Well





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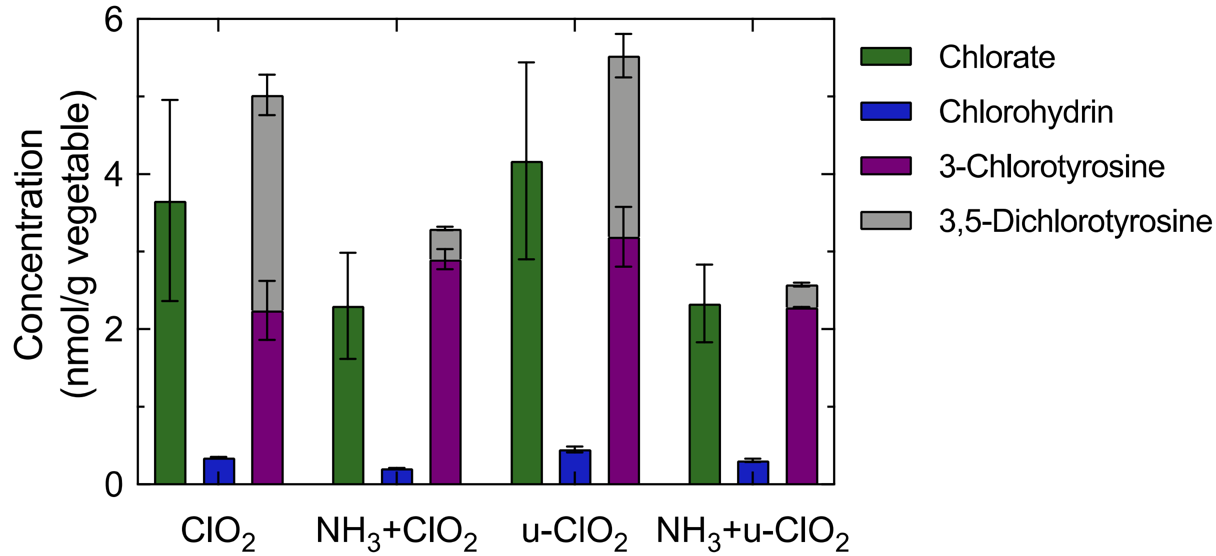
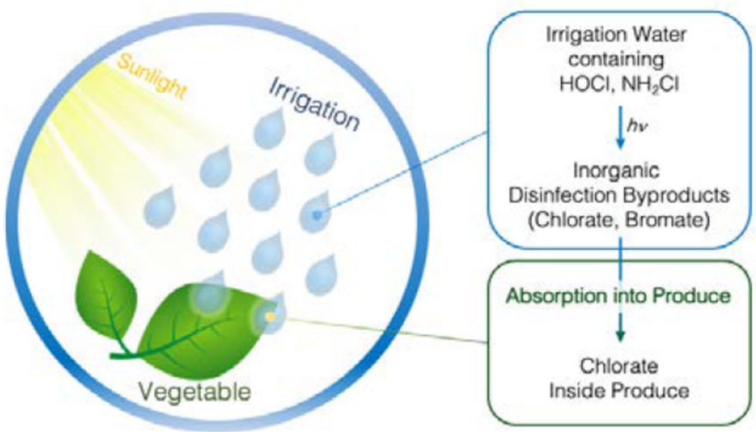
Ammonia can also be Added as a Chlorine Scavenger



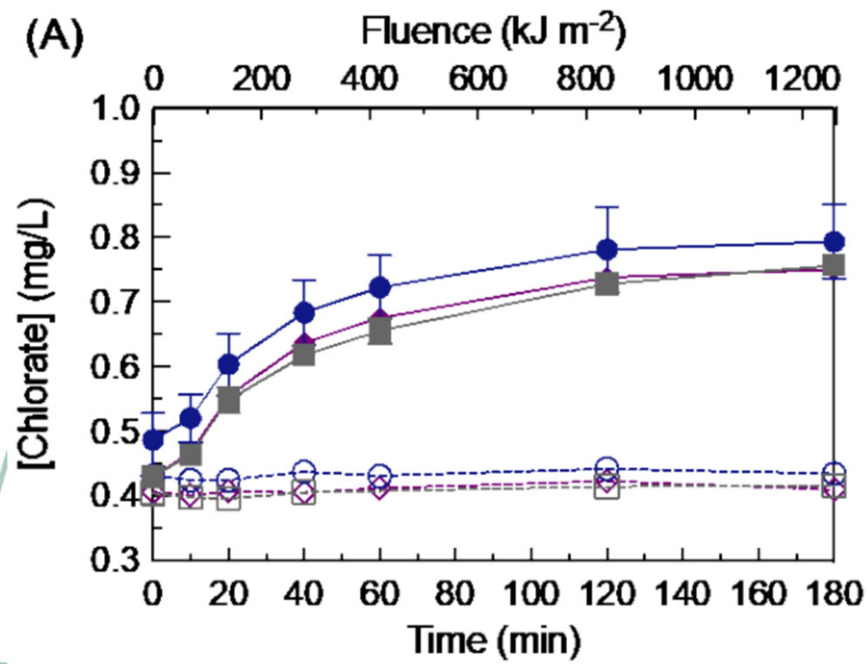
Key Findings from the Mitch Lab

Sunlight-Driven Chlorate Formation During Produce Irrigation with Chlorine- or Chloramine-Disinfected Water

Min-Jeong Suh[1] and William A. Mitch[1,*]



Sunlight Enhances Chlorate Formation in Chlorinated Water



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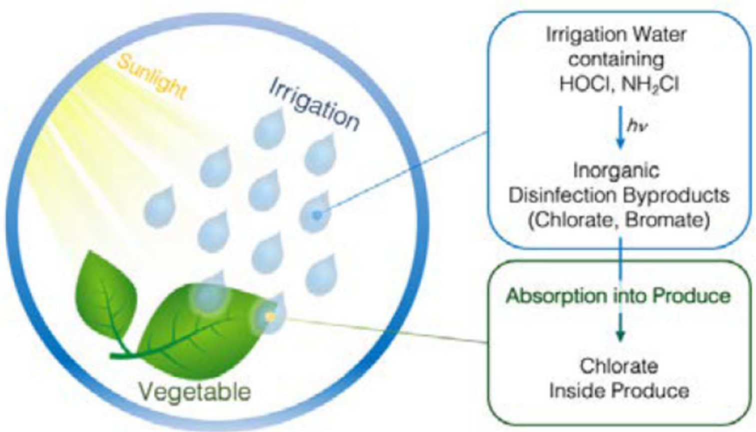
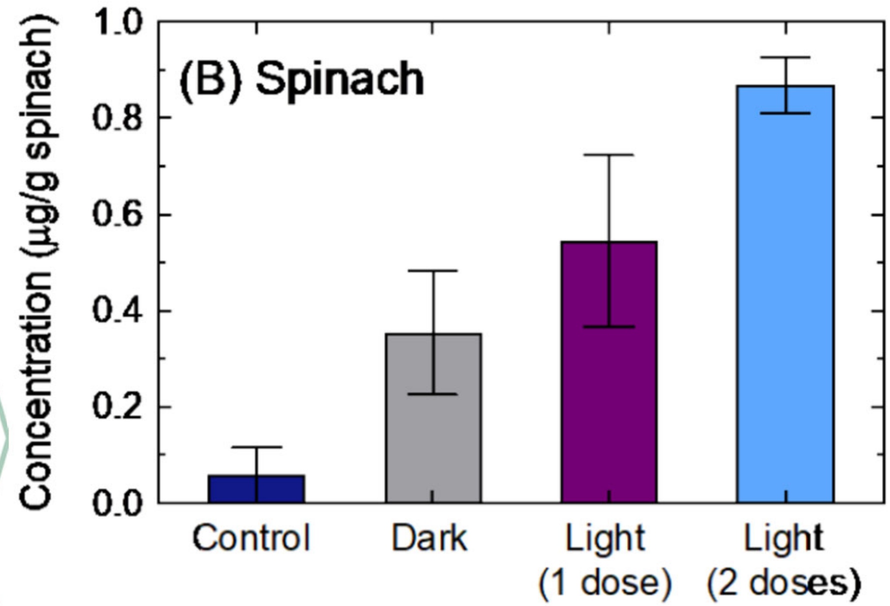


When Sprayed onto Spinach Leaves, the Rate of Chlorate Formation Increased



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Chlorate Residues as a Potential Trade Barrier

Areas of Concern

- Chlorinated Water
  - ~~Rehydration~~ Direct Contact
  - Rinsing
  - Wet Sanitation
- Environmental Factors
  - Sunlight
  - Fruit / Water Temperature
- Old Sanitizing Agents

Recommendations

- Consider Alternatives to Bleach
  - $Ca(OCl)_2$ instead of $NaOCl$
  - Chlorine Dioxide
  - Non-Chlorine Sanitizers
- Test Finished Product
  - Maybe able to Determine "Facility Effect"

THANK YOU!

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