Potential Exposure to Bactericides/Fungicides Designed with Nanomaterials in Vegetable Production for Fresh Consumption in the U.S.

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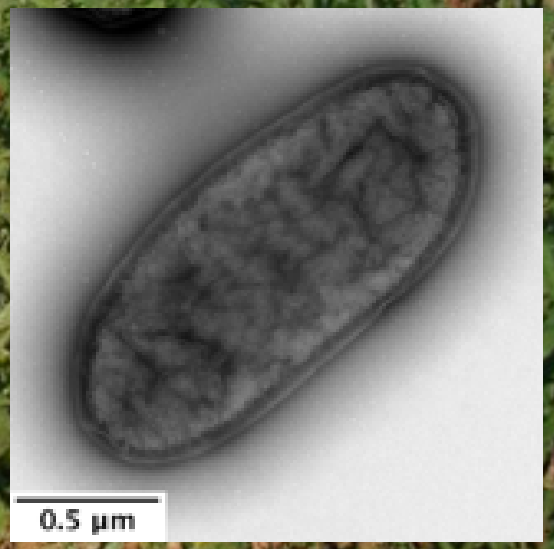
The U.S Fresh Market Tomato Industry (2017): >92,000 acres harvested; >$1.2 billion in value

Bacterial Spot of Tomato - Topmost among bacterial diseases of tomato in the U.S and worldwide



- First discovered in South Africa in 1914
- Caused by 4 distinct species of *Xanthomonas* (*X. euvesicatoria, X. gardneri, X. perforans,* and *X. vesicatoria*). *X. perforans* is the dominant species in Florida
- The disease can cause 20-50% yield losses under ideal conditions for bacterial spread

How does a typical disease management program for bacterial spot (only!) by foliar application on tomato in Florida looks like?

Antibiotics → **1-2 times**: Used during 1950s; continuous field use led to bacterial resistance development. Currently only used in transplant production.

Copper + Mancozeb → **10-20 times:** As of 2006, all *X. perforans* strains (375+) in Florida are copper-tolerant.

SAR Inducers (e.g. Actigard, Leap, Vacciplant) → **6-10 times.** Risks of yield reduction with Actigard

Bacteriophages and other bio-control agents → **5-10 times**: Tank mix or rotation partner as a protectant with all above materials. Effectiveness is inconsistent and environment dependent.

Alternative materials that killed copper tolerant *X. perforans* strains

- TiO_2/Zn and TiO_2/Ag – Photocatalytic nanomaterials killed cells at 500 ppm, but caused phytotoxicity on plants (Partner: Ecoactive Surfaces)
- Ag-ds-DNA-GO nano – Ag nanomaterials killed cells at 13 ppm (Partner: Dr. Weihong Tan)
- Copper composites (copper-core shell silica, copper-multivalent, copper-fixed quat) (Partner: Dr. Swadeshmukul Santra)
- **Metal oxides (MgO & others) - MgO killed cells at 75 ppm - U.S Nano**
- Cu/Zn hybrid - Killed cells at 100 ppm - U.S Nano

In comparison: Conventional copper (Kocide 3000) did not kill cells even at 500-1000 ppm

Lets do a simple math on Cu

- In Florida copper is used as on tomatoes up to 10-20 times in a single season. ~36% of the total Cu sprayed can be found in runoff from plants which contributes to a very high accumulation level of Cu in soil that is detrimental to soil microorganisms, and aquatic organisms (Merrington et al., 2002; Rice et al., 2003).

Kocide 3000 - 27 lb/A (Maximum season rate which corresponds to ~10 lb/A of elemental copper/season (2; 20 lb/A) which comes to ~600,000 lbs of Cu annually (30,000 + acres of tomato).

What does this mean for elemental accumulation in tomatoes (fruits)?

MgO was used as a model material for evaluation

Collaborator: Dr. Jason White

Peel

Treatment	rate	Elemental accumulation in fruits (mg/kg-FW^{w})												
	(µg/ml)	Al	B	Ca	Cu	Fe	K	Mg	Mn	Mo	Na	P	S	Zn
Nano-Cu_2O	1000	0.04*	0.72	81.78	0.64	2.42	2353.60	124.66	1.73	0.02	15.83	232.50	116.95	1.66
Nano-Cu_2O	200	0.06	0.66	75.54	0.52	2.32	2193.72	118.52	1.72	0.03	16.71	234.83	117.43	1.46
Nano-MgO	1000	0.06	0.66	76.07	0.50	2.25	2072.64	112.03	2.29	0.02	14.86	230.96	113.79	1.51
Nano-MgO	200	0.05	0.62	69.43	0.43	2.15	2094.00	94.37	1.68	0.02	14.29	205.72	106.84	1.46
Kocide 3000	2100	0.10	0.83	71.90	0.86*	2.56	2284.95	120.08	2.38	0.02	20.24	249.71	123.46	1.88
Cu-EBDC^{x}		0.09	0.74	67.98	0.82*	2.36	2165.51	113.95	2.21	0.03	19.18	251.01	116.91	1.65
Water (Untreated)		0.08	0.76	73.71	0.55	2.58	2079.83	114.61	1.85	0.02	13.10	215.72	123.28	1.64
Significance (P=0.05)		yes	N.S.	N.S.	yes	N.S.	N.S.	N.S.	N.S.	N.S.	N.S.	N.S.	N.S.	N.S.

Flesh

Treatment	rate	Elemental accumulation in fruits (mg/kg-FW^{w})												
	(µg/ml)	Al	B	Ca	Cu	Fe	K	Mg	Mn	Mo	Na	P	S	Zn
Nano-Cu_2O	1000	0.03	0.64	42.52	0.92	2.90	1984.82	131.16	2.97	0.02	17.16	316.11	123.66	1.88
Nano-Cu_2O	200	0.03	0.63	45.74	0.72	2.40	1951.79	115.65	2.45	0.03	19.63	276.48	113.78	1.53
Nano-MgO	1000	0.05	0.64	50.87	0.73	2.45	1818.84	113.47	3.17	0.02	15.92	273.97	107.05	1.66
Nano-MgO	200	0.04	0.63	55.98	0.69	2.51	1902.14	123.72	2.75	0.02	17.46	252.12	113.87	1.62
Kocide 3000	2100	0.08	0.70	43.65	1.04	3.14	2091.54	134.95	3.49	0.02	24.98	329.50	129.64	1.96
Cu-EBDC^{x}		0.05	0.70	52.05	0.90	2.82	2075.94	137.34	3.90	0.03	24.12	322.98	123.64	1.80
Water (Untreated)		0.10	0.66	56.01	0.88	2.63	1978.23	132.40	2.97	0.02	16.53	268.30	113.52	1.73
Significance (P=0.05)		N.S.	N.S.	N.S.	N.S.	N.S.	N.S.	N.S.	N.S.	N.S.	N.S.	N.S.	N.S.	N.S.

Whole fruit

Treatment	rate	Elemental accumulation in fruits (mg/kg-FW[w])												
	(µg/ml)	Al	B	Ca	Cu	Fe	K	Mg	Mn	Mo	Na	P	S	Zn
Nano-Cu_2O	1000	0.05	0.68	66.26	0.64	2.35	2371.04	120.54	1.84	0.02	15.99	232.60	116.66	1.71
Nano-Cu_2O	200	0.07	0.66	72.26	0.60	2.38	2253.44	118.40	2.13	0.03	18.05	241.52	118.78	1.49
Nano-MgO	1000	0.08	0.66	70.19	0.58	2.26	2053.04	114.03	2.72	0.02	15.63	238.99	110.77	1.57
Nano-MgO	200	0.06	0.65	73.88	0.51	2.10	2031.10	107.87	2.31	0.02	15.66	218.88	108.01	1.54
Kocide 3000	2100	0.12*	0.77	58.82	0.90	2.76	2279.24	123.88	2.65	0.02	23.54	268.36	123.90	1.98
Cu-EBDC[x]		0.07	0.72	59.20	0.79	2.55	2277.98	115.19	2.69	0.03	21.41	264.63	118.44	1.68
Water (Untreated)		0.08	0.69	67.17	0.68	2.58	2109.24	121.03	2.43	0.03	14.60	239.91	116.92	1.64
Significance (P=0.05)		yes	N.S.	N.S.	N.S.	N.S.	N.S.	N.S.	N.S.	N.S.	N.S.	N.S.	N.S.	N.S.

Structural framework from a plant pathologist perspective

IDENTIFY A CLEAR ISSUE, ON WHY NANOTECHNOLOGY?

Copper-tolerance | **Copper load** | **Fungicide resistance**

Nanomaterial design | **Efficacy** | **Fruit, leaf, soil accumulation** | **Impact on non-targets (microbiomes)** | **Trophic transfer**

Occupational safety

Compatibility with other materials, cost-benefit ratio

Kocide 3000 – 27 lb/A (Maximum season rate which corresponds to ~10 lb/A of elemental copper/season (2; 20 lb/A) which comes to ~600,000 lbs of Cu annually (30,000 + acres of tomato).

Hypothetical: With copper-composites effectiveness at 1/5th the concentration to commercial Cu, we can potentially reduce Cu levels in FL tomatoes from **~600,000 lbs to ~240,000 lb** with better bactericidal properties if 50% adoption of a product. Similarly **MgO** can significantly reduce copper load in the environment.

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