Preliminary Analysis of 2017 Crop Data

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William Stringfellow, Ph. D.

Science Advisor

Earth & Environmental Sciences Area

Energy Geosciences

Berkeley National Laboratory

EARTH & ENVIRONMENTAL SCIENCES

UNIVERSITY OF THE PACIFIC

ECOLOGICAL ENGINEERING RESEARCH PROGRAM

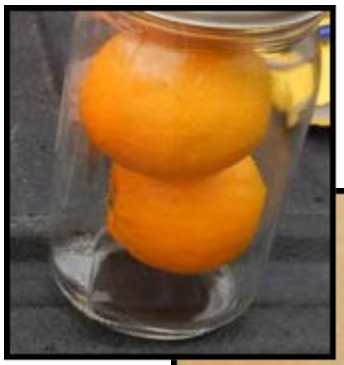
Outline

- Description of sampling and methods
- Preliminary results
- Discussion of results
- Next steps

Sampling Events 2017

- Sample collected by
  - Advanced Environmental Concepts, Inc.
  - Regional Board staff (Kern-Tulare WD, 04/04/17)
- Oversight & sample shipping
  - Regional Board
  - Berkeley National Laboratory
- Analysis conducted by
  - Weck Laboratories
    - State certified environmental laboratory

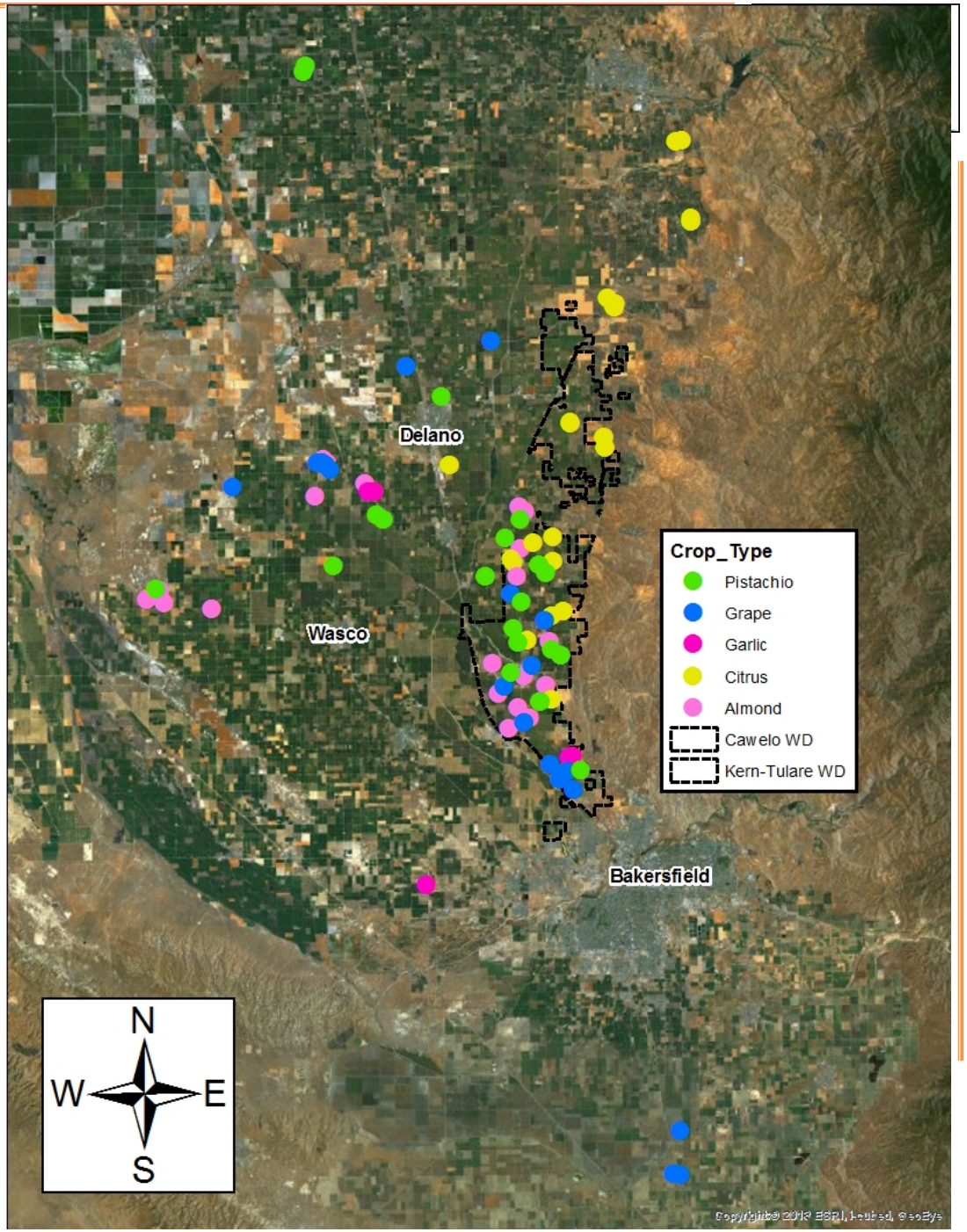
Sampling Events 2017



Date sampled	Crop Sampled
03/29/17	Citrus
03/30/17	Citrus
04/04/17	Citrus
07/18/17	Garlic
08/08/17	Almond, Garlic, Grape
08/09/17	Almond, Grape
08/10/17	Almond, Grape
09/06/17	Pistachio
09/07/17	Pistachio

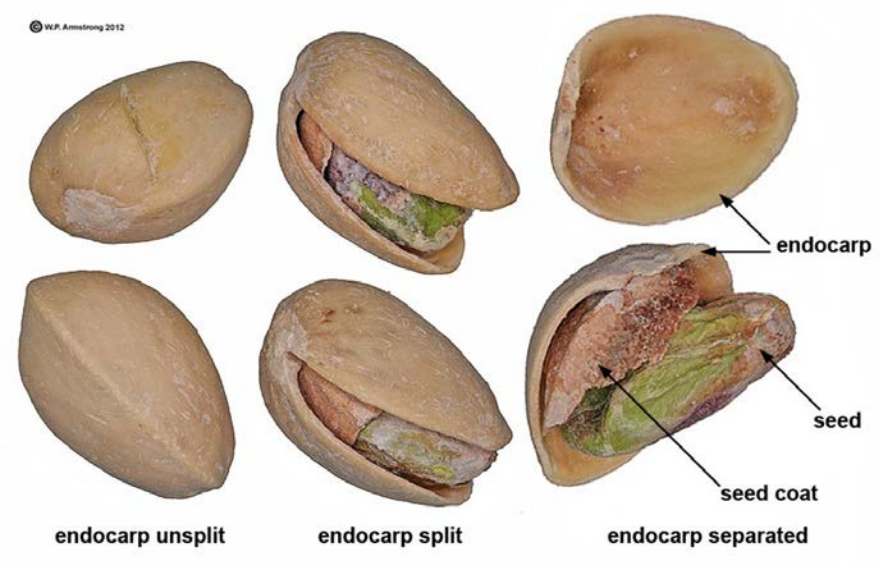
Sampling 2017

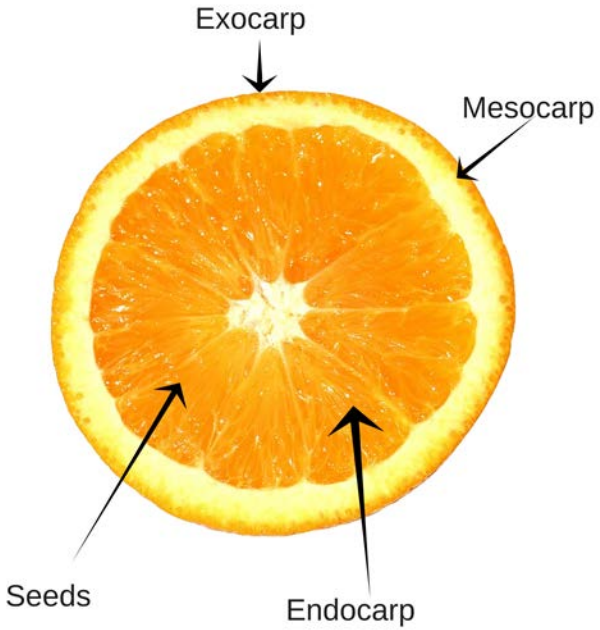
- Samples collected at treated & control sites
  - 110 samples
    - 22 duplicates
- Treated sites receive produced water as part of irrigation supply
- Control sites receive irrigation water from surface & groundwater



Preparation & Analysis

- Fruit samples shipped to certified contract laboratory
  - Weck Laboratories, City of Industry, CA
- Analysis on edible portion of fruit
  - Peeled or shelled in laboratory





http://www2.palomar.edu/users/warmstrong/ecoph8.htm

www.naranjasdelcarmen.com

Preparation & Analysis

- Analysis for known contaminants of concern in petroleum industry
- Organics
  - 26 requested
    - PAHs, BTEX, carbazole, pyridine
    - Acetone, methanol
      - Found in water samples in past monitoring
  - 64 other compounds also analyzed
    - Chlorinated solvents, miscellaneous volatile & semi-volatile organics
- Metals
  - 18 metals
  - Total metal concentrations

Sample Analysis: Organics

- Alcohols by EPA Method 8015D
  - Methanol
- Semivolatile Organic Compounds by EPA Method 8270C
  - Bis(2-ethylhexyl)phthalate, carbazole, phenol, pyridine
- Semivolatile Organics - Low Level by GC/MS SIM Mode Method EPA 8270C SIM
  - PAHs (naphthalene, phenanthrene, etc.)
- Volatile Organic Compounds by EPA Method 8260B
  - BTEX (gasoline hydrocarbons)

Sample Analysis: Metals

- Metals (Non-Aqueous) by EPA 6000/7000 Series
  - Method: EPA 6010B
    - Lithium
  - Method: EPA 6020A & 6020B
    - Antimony, Arsenic, Barium, Beryllium, Cadmium, Chromium, Cobalt, Copper, Lead, Molybdenum, Nickel, Selenium, Silver, Strontium, Thallium, Vanadium, Zinc

List of Organic Analytes Requested

- 1,2,4-Trimethylbenzene
- Acetone
- Benzene
- Ethylbenzene
- Methanol
- Toluene
- o-, m-, and p-Xylene
- 2-Methylnaphthalene
- Acenaphthene
- Acenaphthylene
- Anthracene
- Benzo (a) anthracene
- Benzo (a) pyrene
- Benzo (b) fluoranthene
- Benzo (g,h,i) perylene
- Benzo (k) fluoranthene
- Chrysene
- Dibenzo (a,h) anthracene
- Fluoranthene
- Fluorene
- Indeno (1,2,3-cd) pyrene
- Naphthalene
- Phenanthrene
- Pyrene
- Carbazole
- Pyridine

List of Inorganic Analytes Requested

- Antimony
- Arsenic
- Barium
- Beryllium
- Cadmium
- Chromium (total)
- Cobalt
- Copper
- Lead
- Lithium
- Molybdenum
- Nickel
- Selenium
- Silver
- Strontium
- Thallium
- Vanadium
- Zinc

Preliminary Results

- Measurements made for analysis of 108 organic and inorganic compounds
- Only 16 compounds or elements were detected in any of the crop samples
  - 6 inorganic compound
    - Barium, Copper, Molybdenum, Nickel, Strontium, Zinc
  - 10 organic compounds
    - 1,2,4-Trimethylbenzene, 2-Hexanone, Acetone, Acrolein, Bis(2-ethylhexyl)phthalate, Methanol, Naphthalene, Phenol, p-Isopropyltoluene, sec-Butylbenzene

Preliminary Results

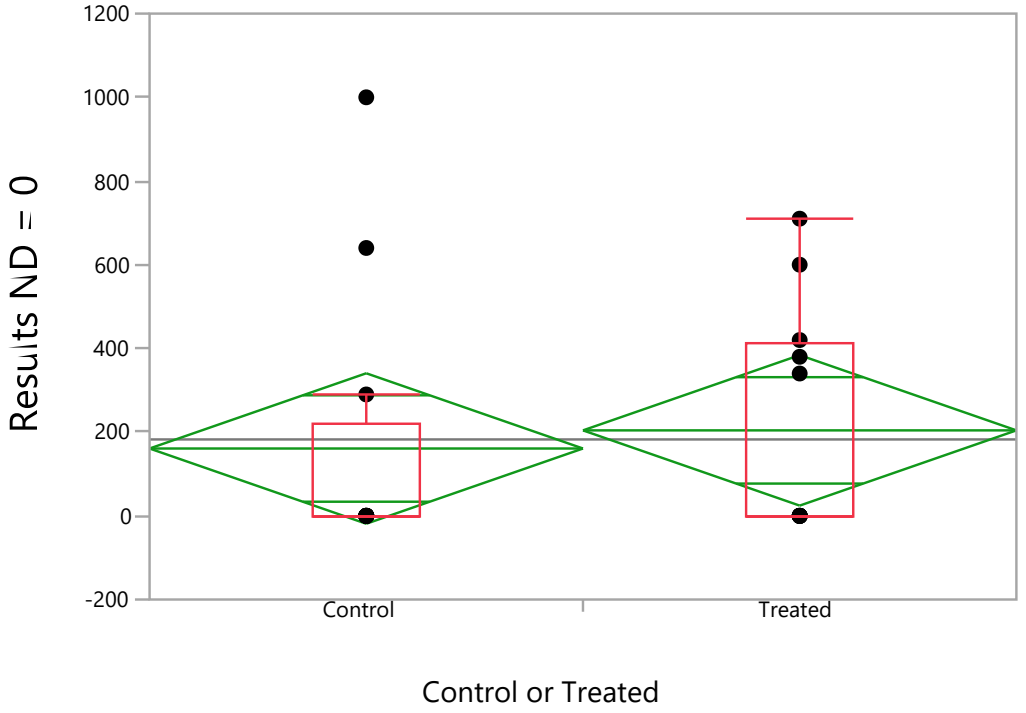
- Organic analytes found, but of low interest in context of oil field food safety study
  - Methanol
    - Only found in control samples (garlic)
  - Phenol
    - Found in one control sample (citrus)
  - sec-Butylbenzene
    - Found in one treated sample (citrus)
  - Bis(2-ethylhexyl)phthalate
    - Garlic (1 control), Grape (1 control & 1 treated), Pistachio (1 treated)

Preliminary Results

- Organic analytes found & discussed previously
  - 1,2,4 trimethylbenzene
    - Found in citrus, treated & controls
    - False positive, interference from terpene
  - Acetone
    - Found in citrus, garlic, pistachio, treated & controls
    - Naturally occurring in fruit
  - p-Isopropyltoluene (p-Cymene)
    - Found in citrus, treated & controls
    - Naturally occurring in fruit
  - Naphthalene
    - False positive with 8260B Method, citrus, treated & controls
    - Not found with 8270C-SIM (specific, high-sensitivity method)

Preliminary Results: 2-Hexanone

- Grapes only
  - Treated and controls
  - Not statistically different
- Detected in 8 out of 24 samples
- Naturally occurring?
- Not on target list



Analysis of Variance

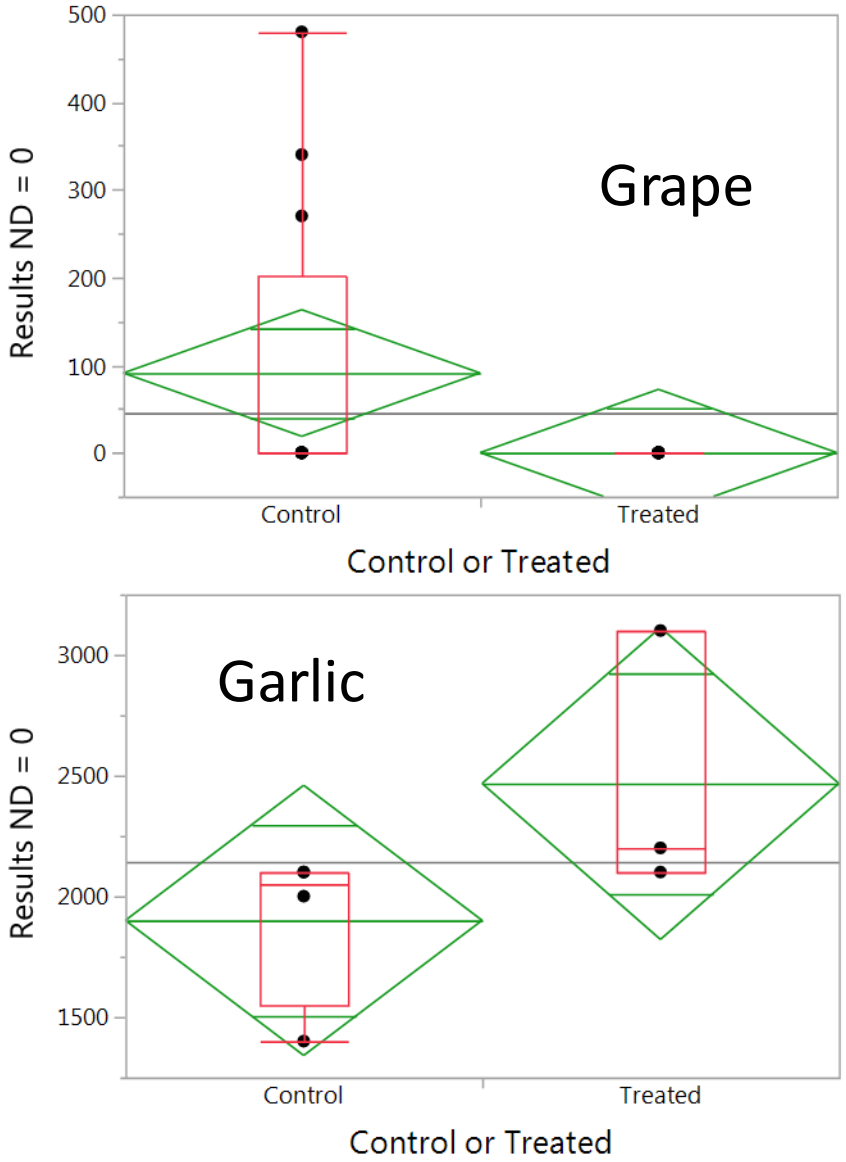
Source	DF	Sum of Squares	Mean Square	F Ratio	Prob > F
Control or Treated	1	11266.7	11266.7	0.1250	0.7271
Error	22	1983583.3	90162.9		
C. Total	23	1994850.0			

Means for Oneway Anova

Level	Number	Mean	Std Error	Lower 95%	Upper 95%
Control	12	160.833	86.681	-18.93	340.60
Treated	12	204.167	86.681	24.40	383.93

Preliminary Results: Acrolein

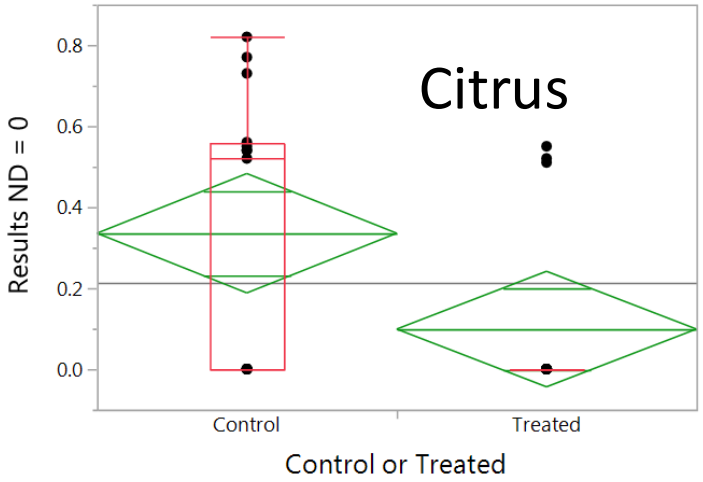
- Grapes
  - Control only
    - 3 of 24 samples
- Garlic
  - Treated and controls
    - 7 of 7 samples
  - Not statistically different
- Naturally occurring?

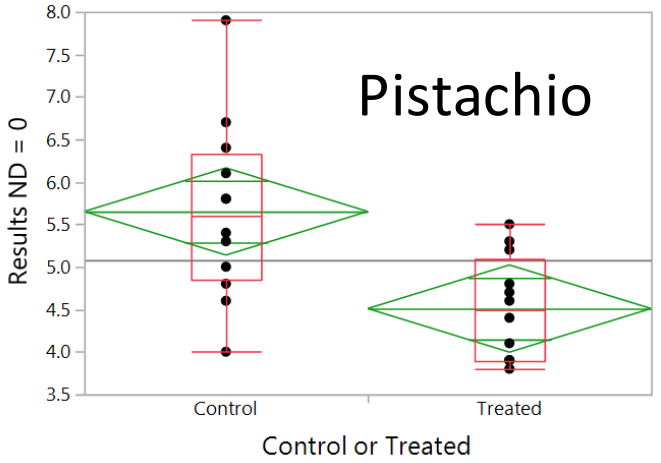


Preliminary Results: Copper

- Trace nutrient
  - Needed for growth

Crop Type		No. Samp.	No. Det.	Mean (mg/kg)	Std. Dev.	Sig. Dif.
Almond	Control	12	12	7.3	1.7	No
Almond	Treated	12	12	7.4	1.2	
Citrus	Control	15	8	0.3	0.3	Yes
Citrus	Treated	16	3	0.1	0.2	
Garlic	Control	4	4	2.3	0.3	No
Garlic	Treated	3	3	2.4	0.1	
Grape	Control	12	12	2.0	1.4	No
Grape	Treated	12	12	1.4	1.1	
Pistachio	Control	12	12	5.7	1.1	Yes
Pistachio	Treated	12	12	4.5	0.6	





Preliminary Results: Molybdenum

- Trace nutrient
  - Needed for growth

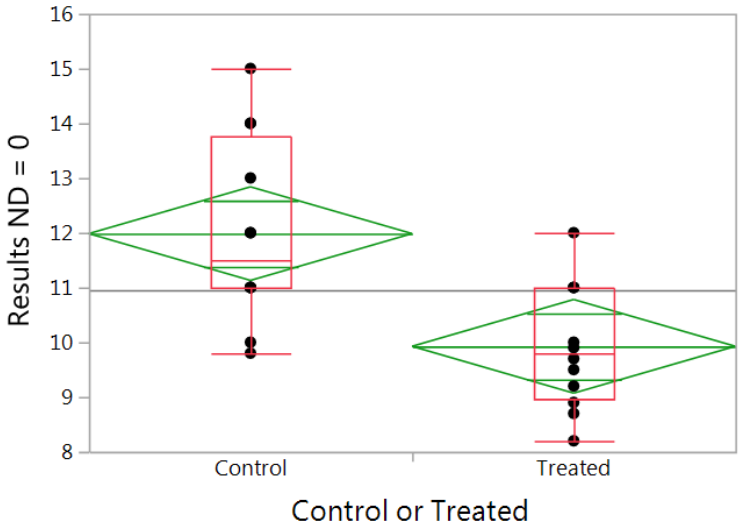
Crop Type		No. Samp.	No. Det.	Mean (mg/kg)	Std. Dev.	Sig. Dif.
Almond	Control	12	1	0.0	0.1	No
Almond	Treated	12	1	0.0	0.2	
Citrus	Control	15	0	0.0	0.0	No
Citrus	Treated	16	0	0.0	0.0	
Garlic	Control	4	0	0.0	0.0	No
Garlic	Treated	3	1	0.2	0.4	
Grape	Control	12	0	0.0	0.0	No
Grape	Treated	12	0	0.0	0.0	
Pistachio	Control	12	1	0.1	0.2	No
Pistachio	Treated	12	0	0.0	0.0	

Preliminary Results: Zinc

- Trace nutrient
  - Needed for growth

Crop Type		No. Samp.	No. Det.	Mean (mg/kg)	Std. Dev.	Sig. Dif.
Almond	Control	12	12	22.7	7.7	No
Almond	Treated	12	12	22.8	6.0	
Citrus	Control	15	0	0.0	0.0	No
Citrus	Treated	16	0	0.0	0.0	
Garlic	Control	4	4	12.0	0.0	No
Garlic	Treated	3	3	11.0	0.0	
Grape	Control	12	0	0.0	0.0	No
Grape	Treated	12	0	0.0	0.0	
Pistachio	Control	12	12	12.0	1.7	Yes
Pistachio	Treated	12	12	9.9	1.1	

Pistachio

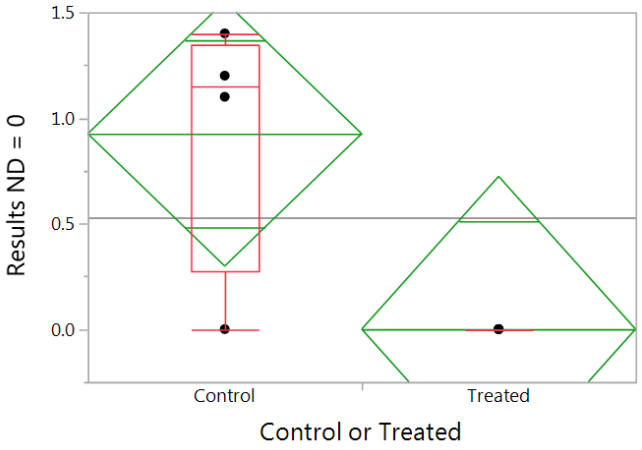


Preliminary Results: Nickel

- Trace nutrient
  - Needed for growth

Crop Type		No. Samp.	No. Det.	Mean (mg/kg)	Std. Dev.	Sig. Dif.
Almond	Control	12	3	0.3	0.5	No
Almond	Treated	12	2	0.2	0.5	
Citrus	Control	15	0	0.0	0.0	No
Citrus	Treated	16	0	0.0	0.0	
Garlic	Control	4	3	0.9	0.6	Yes
Garlic	Treated	3	0	0.0	0.0	
Grape	Control	12	0	0.0	0.0	No
Grape	Treated	12	0	0.0	0.0	
Pistachio	Control	12	1	0.1	0.3	No
Pistachio	Treated	12	0	0.0	0.0	

Garlic

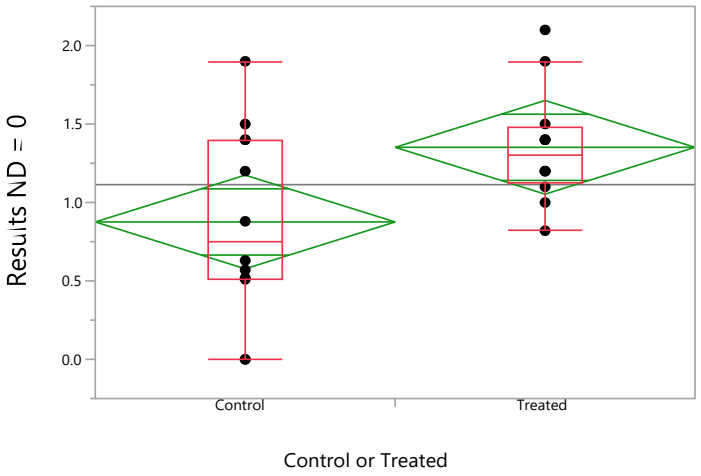


Preliminary Results: Barium

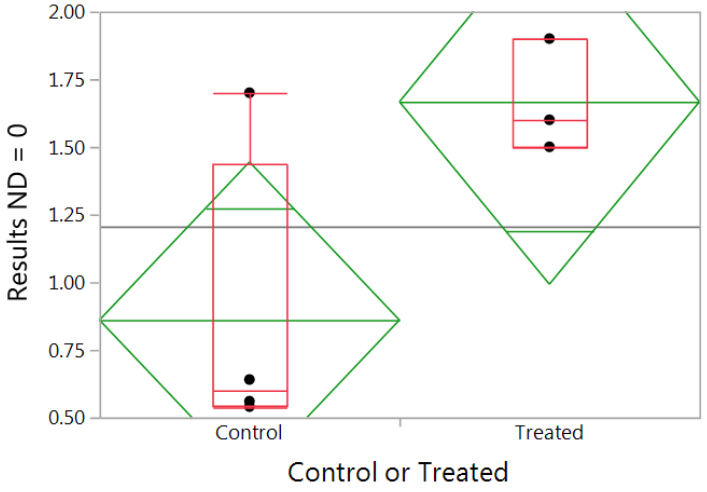
- Natural element
  - Not an essential nutrient

Crop Type		No. Samp.	No. Det.	Mean (mg/kg)	Std. Dev.	Sig. Dif.
Almond	Control	12	10	0.9	0.6	Yes
Almond	Treated	12	12	1.4	0.4	
Citrus	Control	15	7	0.4	0.4	No
Citrus	Treated	16	6	0.3	0.4	
Garlic	Control	4	4	0.9	0.6	Yes
Garlic	Treated	3	3	1.7	0.2	
Grape	Control	12	0	0	0	No
Grape	Treated	12	0	0	0	
Pistachio	Control	12	2	0.1	0.3	Yes
Pistachio	Treated	12	7	0.4	0.4	

Almond



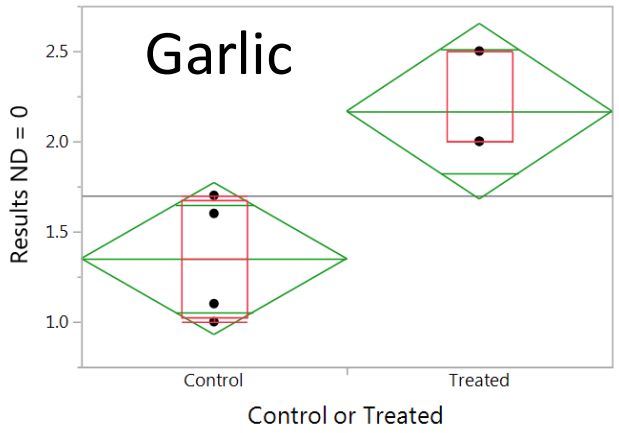
Garlic

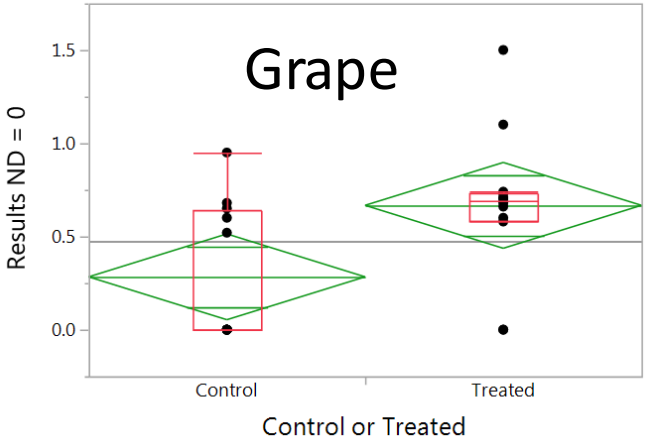


Preliminary Results: Strontium

- Natural element
  - Not an essential nutrient

Crop Type		No. Samp.	No. Det.	Mean (mg/kg)	Std. Dev.	Sig. Dif.
Almond	Control	12	12	6.8	2.9	No
Almond	Treated	12	12	7.0	1.7	
Citrus	Control	15	15	1.8	0.8	Yes
Citrus	Treated	16	16	2.4	0.8	
Garlic	Control	4	4	1.4	0.4	Yes
Garlic	Treated	3	3	2.2	0.3	
Grape	Control	12	5	0.3	0.4	Yes
Grape	Treated	12	10	0.7	0.4	
Pistachio	Control	12	12	1.8	0.5	No
Pistachio	Treated	12	12	2.0	0.8	





Barium & Strontium Context

- There is nothing alarming about the concentration of barium & strontium found in crops
- All concentrations of all compounds tested were within acceptable ranges for safe consumption

Crop	Element	Control Mean Conc. (mg/kg)	Treated Mean Conc. (mg/kg)	Risk-Based Comparison (RBC) Level (mg/kg)*	Times lower
Citrus	Barium	0.6	0.51	3,000	5,405
Citrus	Strontium	2.22	2.8	8,900	3,546
Grape	Barium	ND	ND	2,000	---
Grape	Strontium	0.51	0.9	6,000	8,511
Garlic	Barium	1.44	2.34	3,600	1,905
Garlic	Strontium	1.77	2.65	11,000	4,977
Almond	Barium	1.17	1.65	11,000	7,801
Almond	Strontium	8.23	8.42	34,000	4,084
Pistachio	Barium	0.33	0.65	11,000	22,449
Pistachio	Strontium	2.17	2.39	34,000	14,912

Risk-Based Comparison (RBC) Levels

- Allowable concentrations of each chemical in the edible portion of crop that is protective of human health
  - Concentration considered "acceptable" by regulatory agencies
- Concentrations below RBC levels should not cause adverse health effects (cancerous or non-cancerous)
- Provides very conservative estimates
- RBC Levels are calculated using standard U.S. EPA equations and factors
  - Body weights
  - Exposure frequencies and durations
  - Crop ingestion rates
  - Toxicity factors (chronic cancer and non-cancer values)
- Assumes 100% of crop ingestion is from an impacted source
- Does not take into account the potential for an individual to consume multiple different impacted crop types

Barium & Strontium Context

- Barium & strontium are naturally occurring elements
- Differences in treated & control crops could be reflective of natural differences in soils at the different areas
- Could be effect of agricultural practices
- Could be natural variation
  - Nickel, zinc, copper were higher in control areas
- Could be (subtle) effect from different source waters
  - Not necessarily produced water

Next Steps

- Complete a full second year of sampling & analysis
  - Almonds, citrus, garlic, grape, pistachio
  - Two full years of independent data (2017 & 2018)
- Investigate soil conditions & other factors potentially influencing elemental concentrations
  - GIS analysis & water chemistry using existing data
  - Soil studies under consideration, if warranted
- Continue investigation of oil field chemicals as potential organic contaminates in fruit
  - New disclosure information

Next Steps

- Start “MOU” projects
- Task 1: Selection of Chemicals of Interest for Further Evaluation
  - Needed to insure full evaluation is conducted
  - Needed for analysis of oil field disclosures
- Task 2: Literature Review for Produced Water Reuse in Agriculture
  - Includes more complete evaluation of chemical in crops

Contact information

Will Stringfellow

Wstringfellow@lbl.gov

Funding acknowledgement:
California State Water Resources Control Board
University of the Pacific Ecological Engineering Research Program

EXTRA SLIDES FOLLOW

References

- US EPA (2017) Food Commodity Intake Database 2005-2010 http://fcid.foodrisk.org/percentiles
- Office of Environmental Health Hazard Assessment (OEHHA). Chemicals Database. https://oehha.ca.gov/chemicals
- US EPA (2017) Regional Screening Levels (RSLs) – Generic Tables. https://www.epa.gov/risk/regional-screening-levels-rsls-generic-tables-november-2017
- US EPA (2011) Exposure Factors Handbook: 2011 Edition. https://cfpub.epa.gov/ncea/risk/recordisplay.cfm?deid=236252#tab-3

References

- ATSDR 2007, Toxicological Profile for Barium & Barium Compounds
- ATSDR 2004, Toxicological Profile for Copper
- ATSDR 2004, Toxicological Profile for Strontium
- ATSDR 1994, Toxicological Profile for Acetone
- OEHHA 2000, Proposed Action Levels for sec-Butylbenzene and tert-Butylbenzene
- NIH PubChem Database 2017, p-Cymene (p-Isopropyltoluene)
- NIH PubChem Database 2017, D-Limonene
- Haminiuk, C.W.I. et al. 2012, Phenolic compounds in fruits – an overview, *Intern. J. Food Sci. and Technol.*, 47, 2023–2044

- NIH = National Institute of Health
- OEEHA = Office of Environmental Health Hazard Assessment (California Department of Health Services)
- ATSDR = Agency for Toxic Substances and Disease Registry (U.S. Public Health Service)

Data

- 95% Upper Confidence Level (UCL) of mean crop chemical concentrations are reported as a standard conservative estimate of mean concentration
- All concentration values are in mg of chemical per kg crop wet weight
- RBC level values have not been peer-reviewed, and should not be used for purposes other than for this study

Barium, Total

Crop	Control Mean (mg/kg)	Treated Mean (mg/kg)	MRL* (mg/kg/day)	Consumption to meet MRL (kg/day)	US Per Capita Consumption (kg/day)
Citrus	0.37	0.29	0.2	48.07	0.0710
Grape	ND	ND	0.2	-	0.0554
Almond	0.88	1.35	0.2	10.36	0.0079
Pistachios	0.12	0.44	0.2	32.06	0.0366
Garlic	0.86	1.67	0.2	8.40	0.0006

ND = not detected

*Intermediate and chronic oral exposure

Reference: Agency for Toxic Substances and Disease Registry (2017). Minimal Risk Levels (MRLs). https://www.atsdr.cdc.gov/mrls/pdfs/atsdr_mrls.pdf

Strontium, Total

Crop	Control Mean (mg/kg)	Treated Mean (mg/kg)	MRL* (mg/kg/day)	Consumption to meet MRL (kg/day)	US Per Capita Consumption (kg/day)
Citrus	1.80	2.39	2	58.64	0.0710
Grape	0.28	0.67	2	210.00	0.0554
Almond	6.79	6.98	2	20.05	0.0079
Pistachios	1.79	2.01	2	69.71	0.0366
Garlic	1.35	2.17	2	64.62	0.0006

*Intermediate oral exposure

Reference: Agency for Toxic Substances and Disease Registry (2017). Minimal Risk Levels (MRLs). https://www.atsdr.cdc.gov/mrls/pdfs/atsdr_mrls.pdf