



Analytical Results of Citrus Sampling March – April 2017

FSP June 28, 2017

William Stringfellow, Ph. D.
Science Advisor

Earth & Environmental Sciences Area
Energy Geosciences
Berkeley National Laboratory



**EARTH &
ENVIRONMENTAL
SCIENCES**





Introduction

- Objectives of March – April sampling
- Methods
 - Sampling
 - Analytes
- Results
- Next steps

Objectives



- Collect citrus samples from current season
 - Required immediate action
- Analyze samples for known chemicals of concern
- Archive samples for later study or repeat analysis

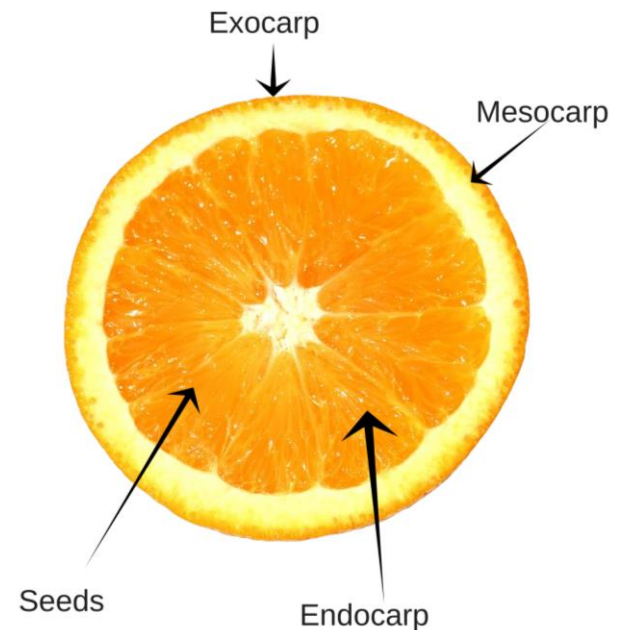
Sampling



- Collected samples March 29-30, April 4
 - Irrigated with some produced water (PW)
 - Not irrigated with any PW (Control locations)
- Samples collected by contract sampler or Regional Board staff
 - Regional Board oversight of sampling & shipping
- Sample composite from at least 3 trees each location
 - Mandarin, Naval, Valencia, lemons

Sampling (continued)

- Fruit samples shipped to certified contract laboratory
- Analysis on edible portion of fruit
 - Peeled in laboratory
- Contract analysis for known contaminants of concern in petroleum industry
 - PAHs, BTEX, heavy metals
- Compounds found in PW
 - Methanol, acetone, chloroform



Analytes

- 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



- Weck Laboratories, City of Industry, CA
- 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
 - Antimony, Arsenic, Barium, Beryllium, Cadmium, Chromium, Cobalt, Copper, Molybdenum, Selenium, Silver, Strontium, Thallium, Zinc
 - Method: EPA 6020B
 - Lead, Nickel, Vanadium

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



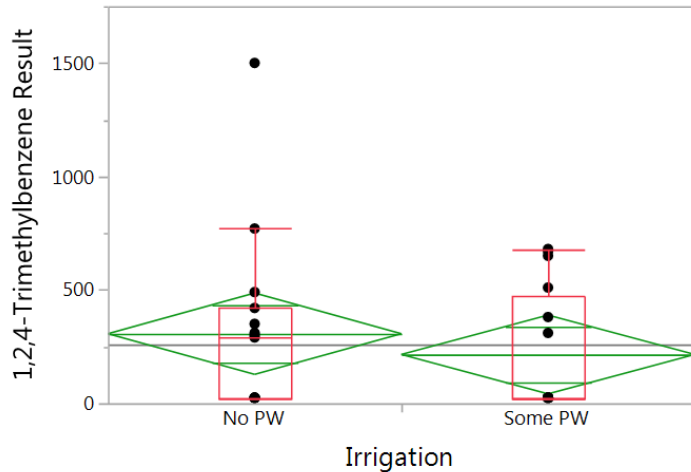
- Antimony
- Arsenic
- Barium
- Beryllium
- Cadmium
- Chromium (total)
- Cobalt
- Copper
- Lead
- Lithium
- Molybdenum
- Nickel
- Selenium
- Silver
- Strontium
- Thallium
- Vanadium
- Zinc

Results Organic

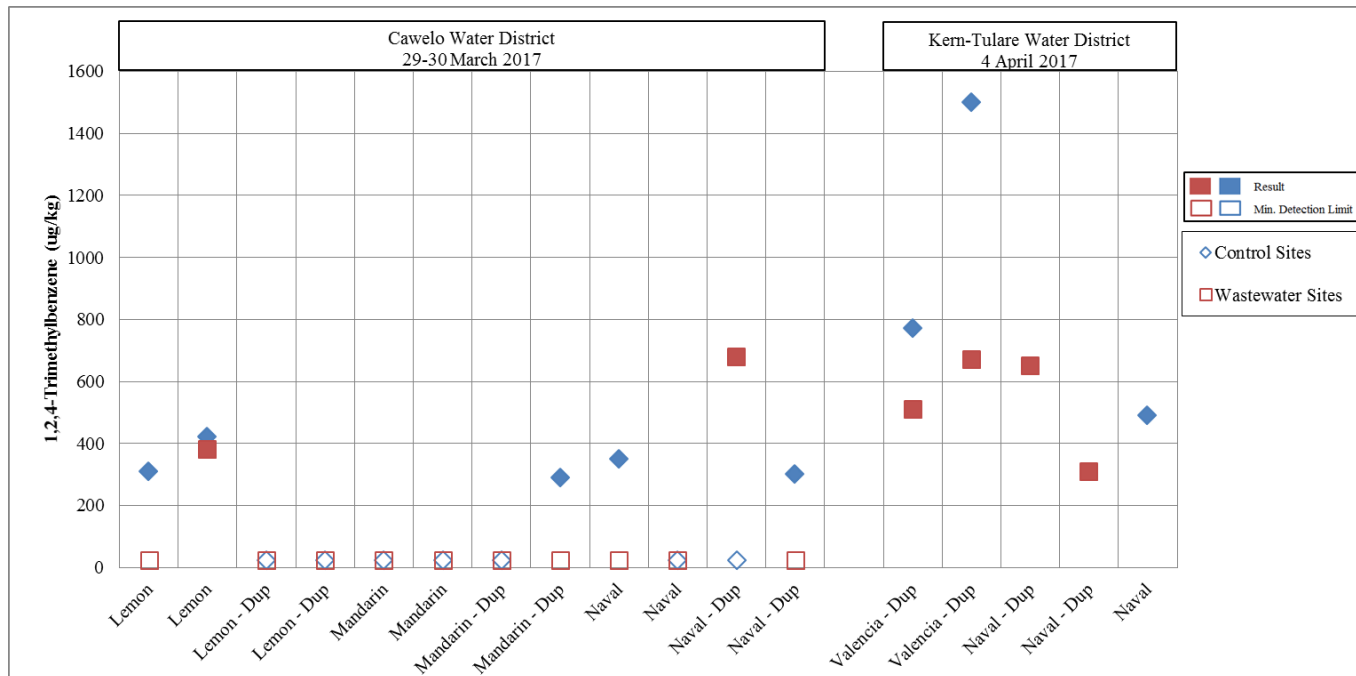


- Organic analytes with measurable detections
 - 1,2,4 trimethylbenzene
 - False positive, interference from terpene
 - Acetone
 - Naturally occurring in fruit
 - p-Isopropyltoluene (p-Cymene)
 - Naturally occurring
 - Phenol
 - Found in one sample (control)
 - sec-Butylbenzene
 - Found in one sample of (PW irrigated)

1,2,4 - Trimethylbenzene



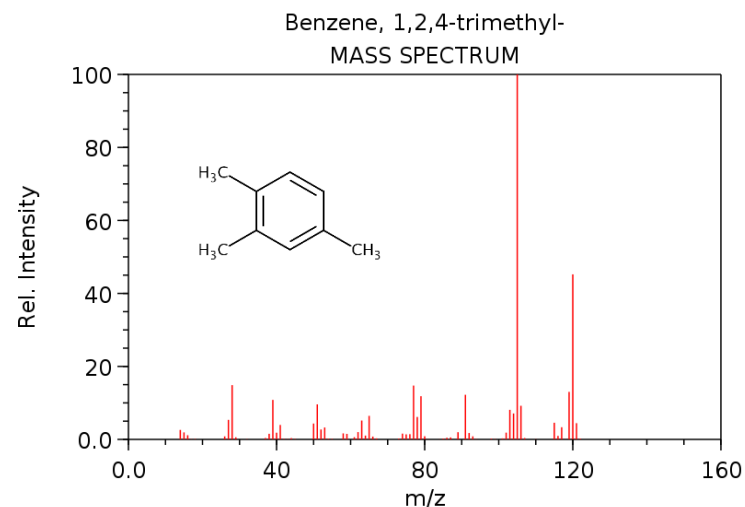
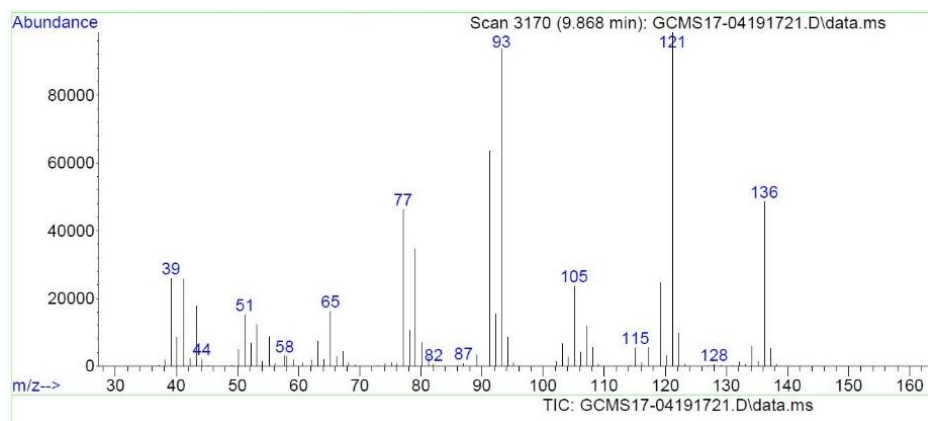
- Not statistically different between PW irrigated and controls that were not PW irrigated



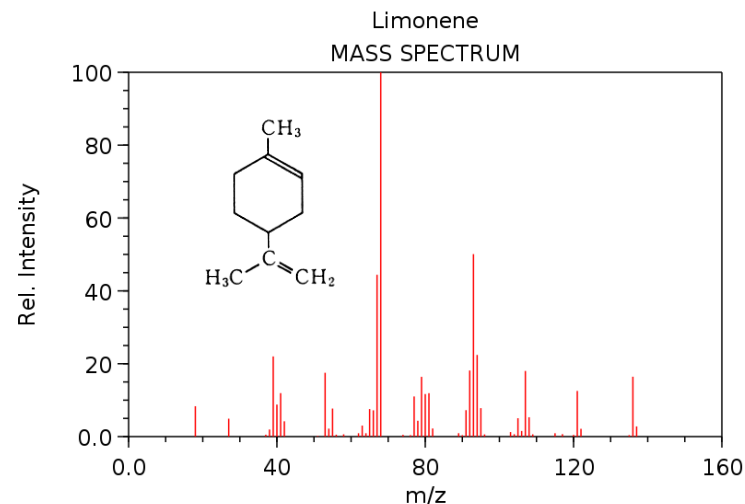
False Positive (Trimethylbenzene)



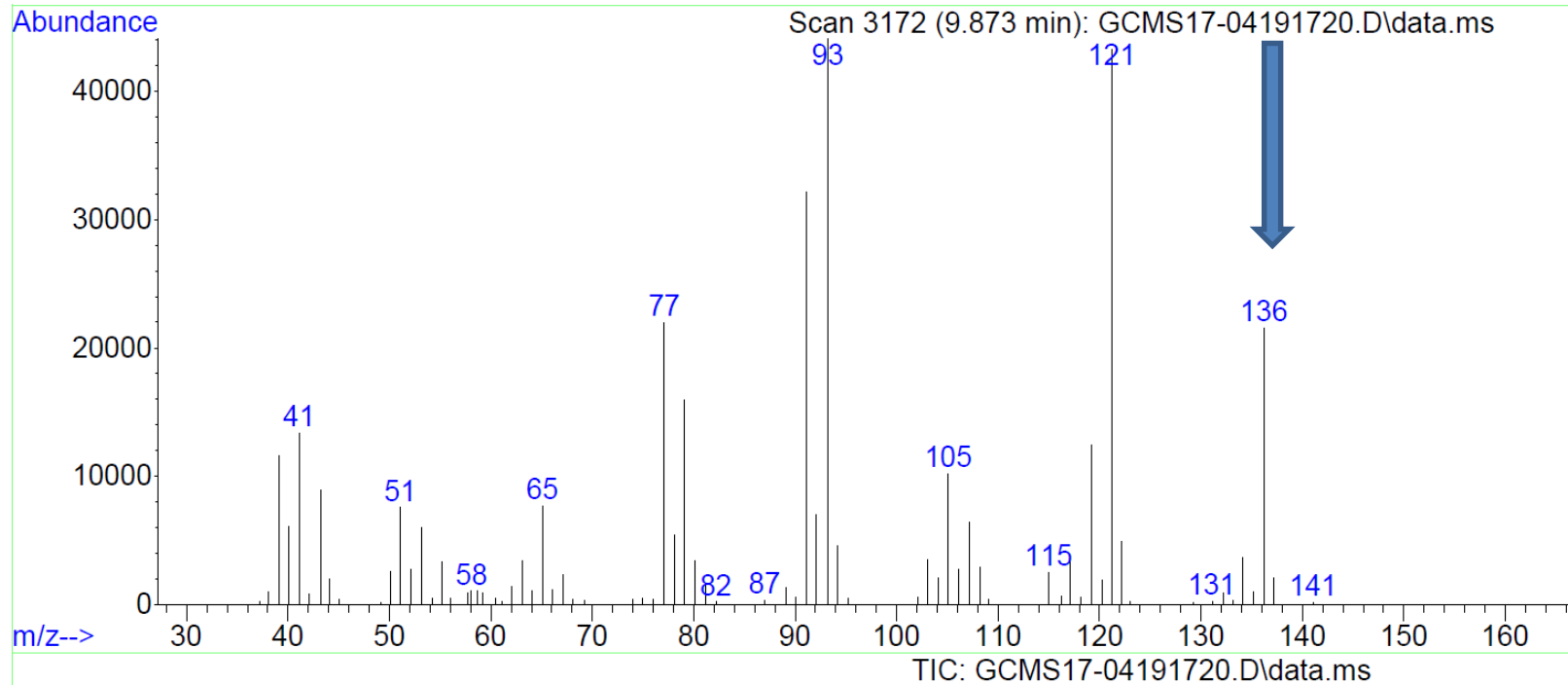
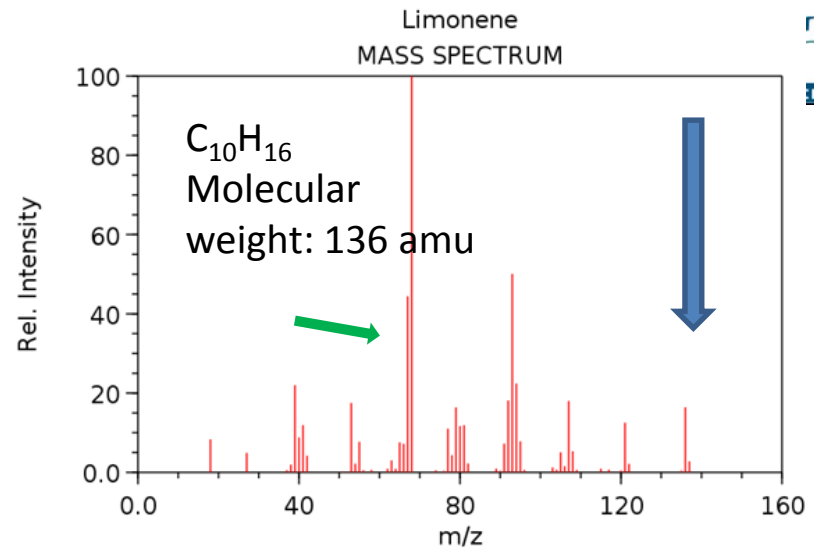
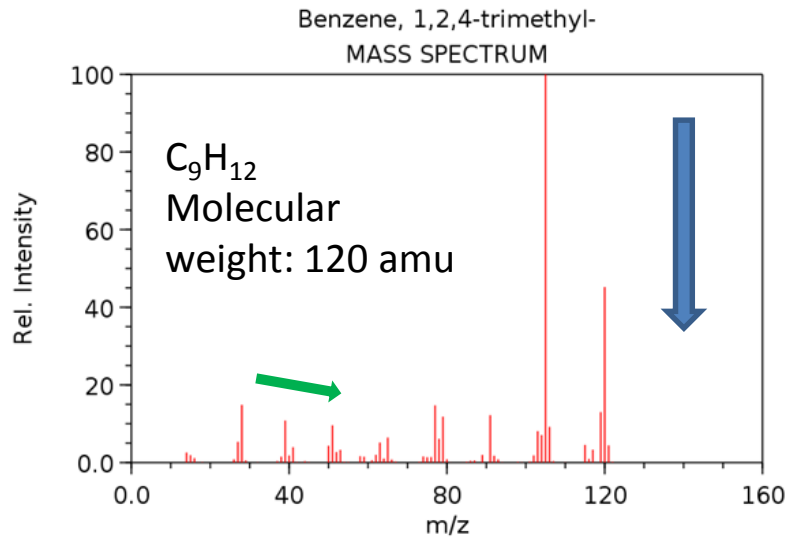
- 124-TMB
 - Molecular weight = 120 g/mol
 - Peaks at 120 & 105 m/z
 - Ratio 43/100
- Limonene
 - Molecular weight = 136 g/mol
 - Monoterpene
 - Natural component of fruit



NIST Chemistry WebBook (<http://webbook.nist.gov/chemistry>)



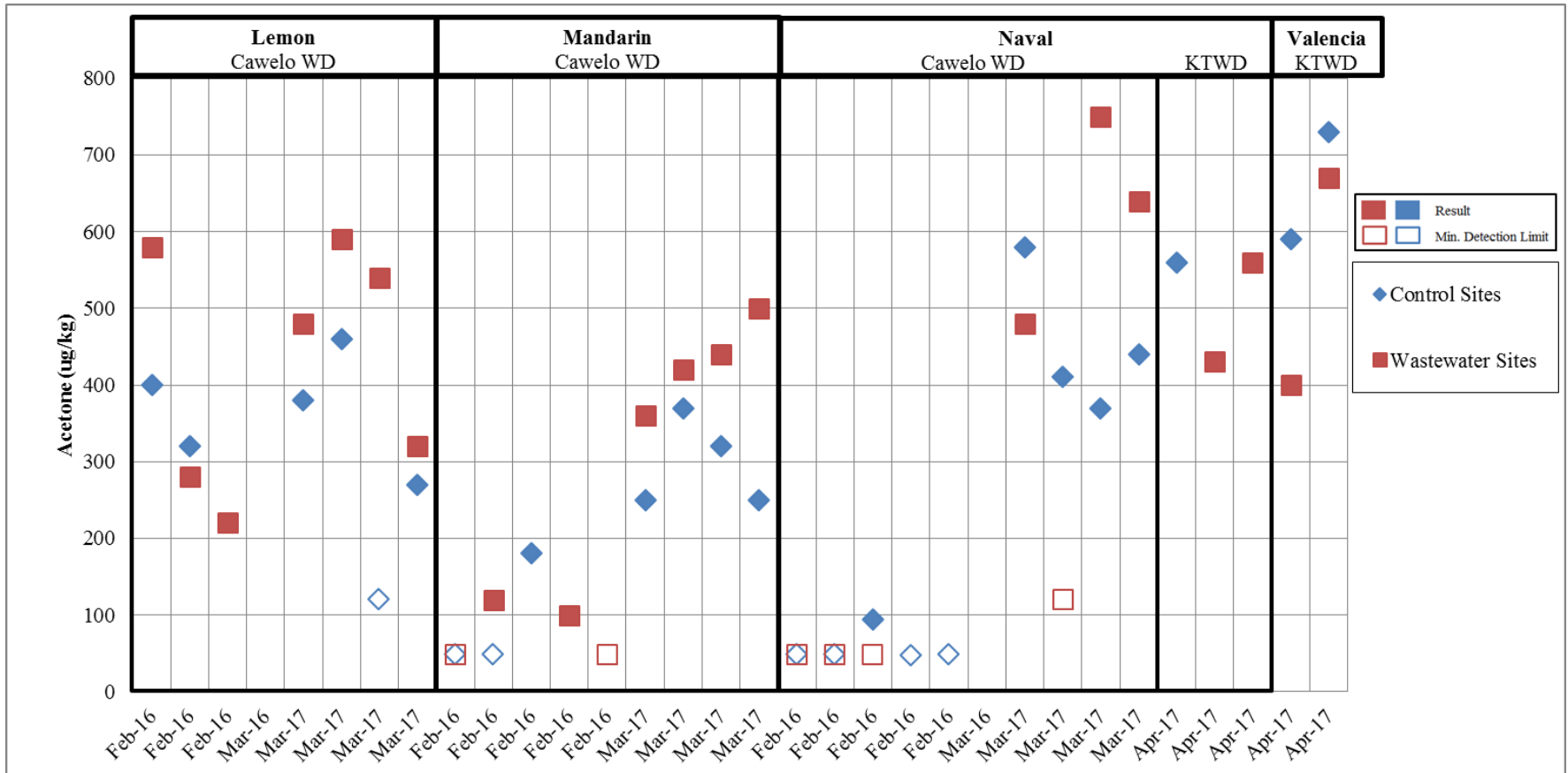
NIST Chemistry WebBook (<http://webbook.nist.gov/chemistry>)



Acetone

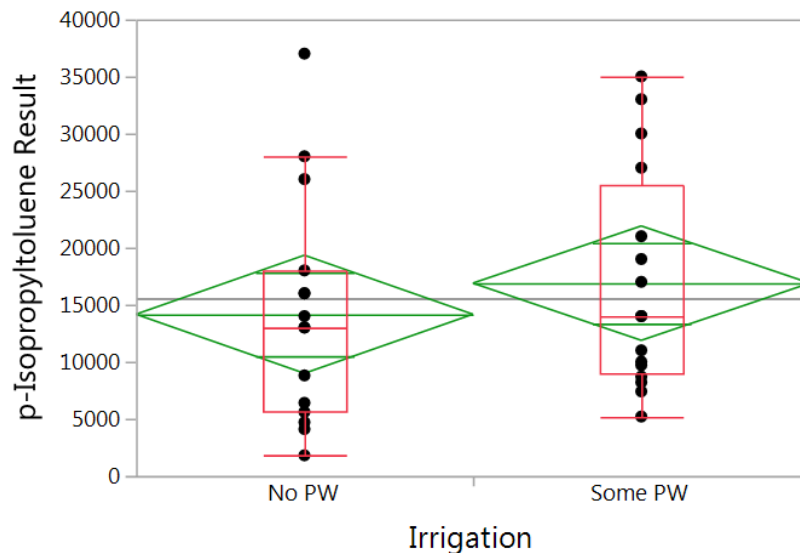
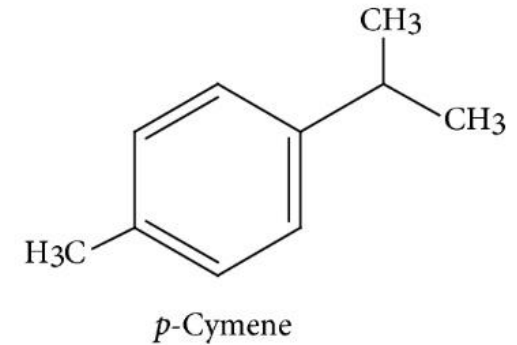
- Found in both PW irrigated & controls
- Naturally occurring in fruit (ATSDR* 1994)

*Agency for Toxic Substances and Disease Registry



p-Isopropyltoluene

- p-Isopropyltoluene
 - Known as p-Cymene
 - Related to terpenes (like limonene)
 - Natural occurring in plants (NIH 2017)
- Found in equal concentrations in PW irrigated & controls



t Ratio	0.774261
DF	29
Prob > t	0.4450
Prob > t	0.2225
Prob < t	0.7775

Other Organics Detected

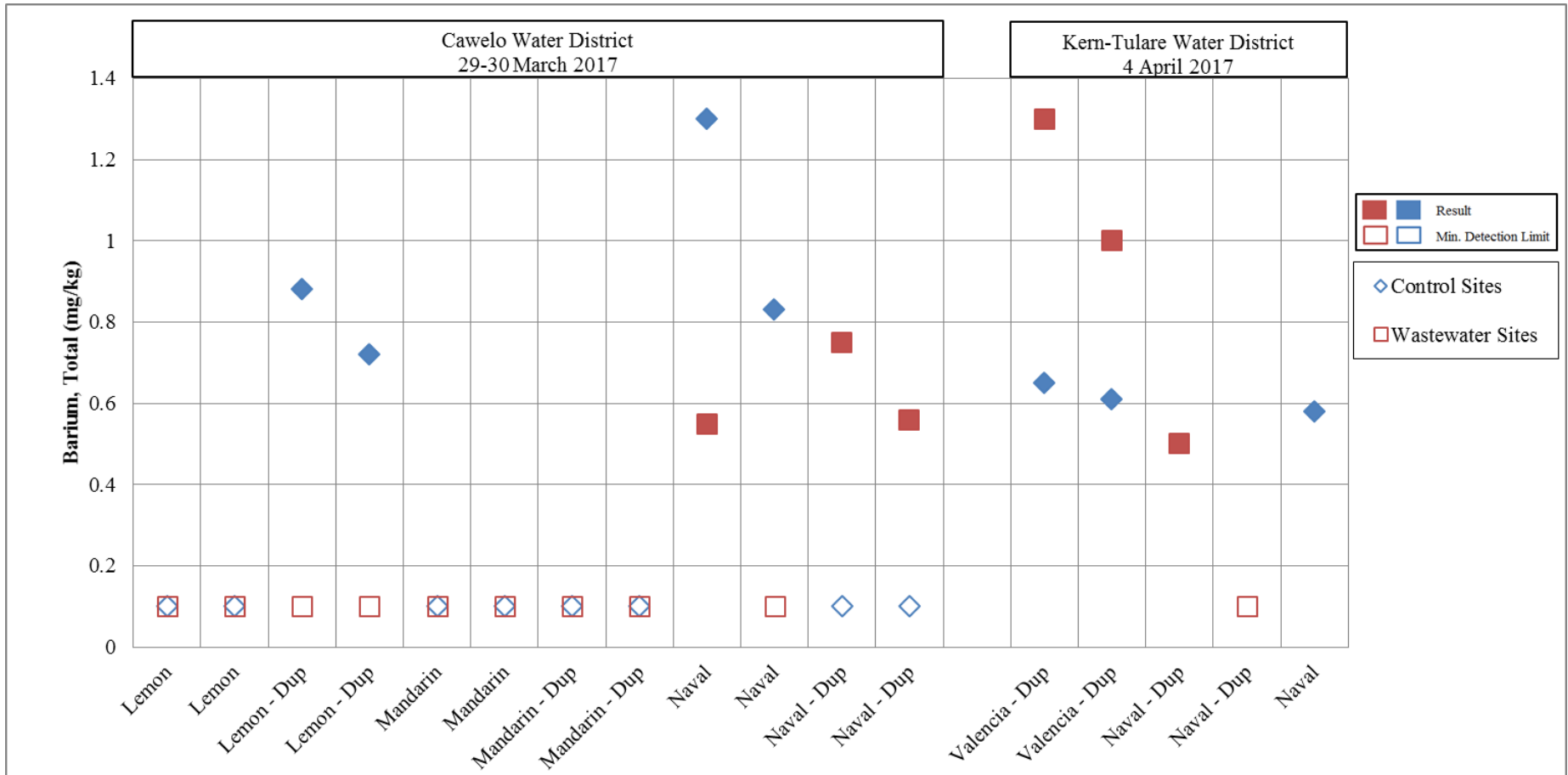


- Phenol
 - One sample only (0.65 mg/Kg)
 - Control sample (Valencia)
 - Phenols occur naturally in fruit (Haminiuk 2012)
 - Antioxidants
- sec-Butylbenzene
 - One sample only, at quantitation limit
 - PW irrigated sample (Mandarin)
 - N-butyl benzene found in cooked fruit (pies)
 - False positive?

Barium



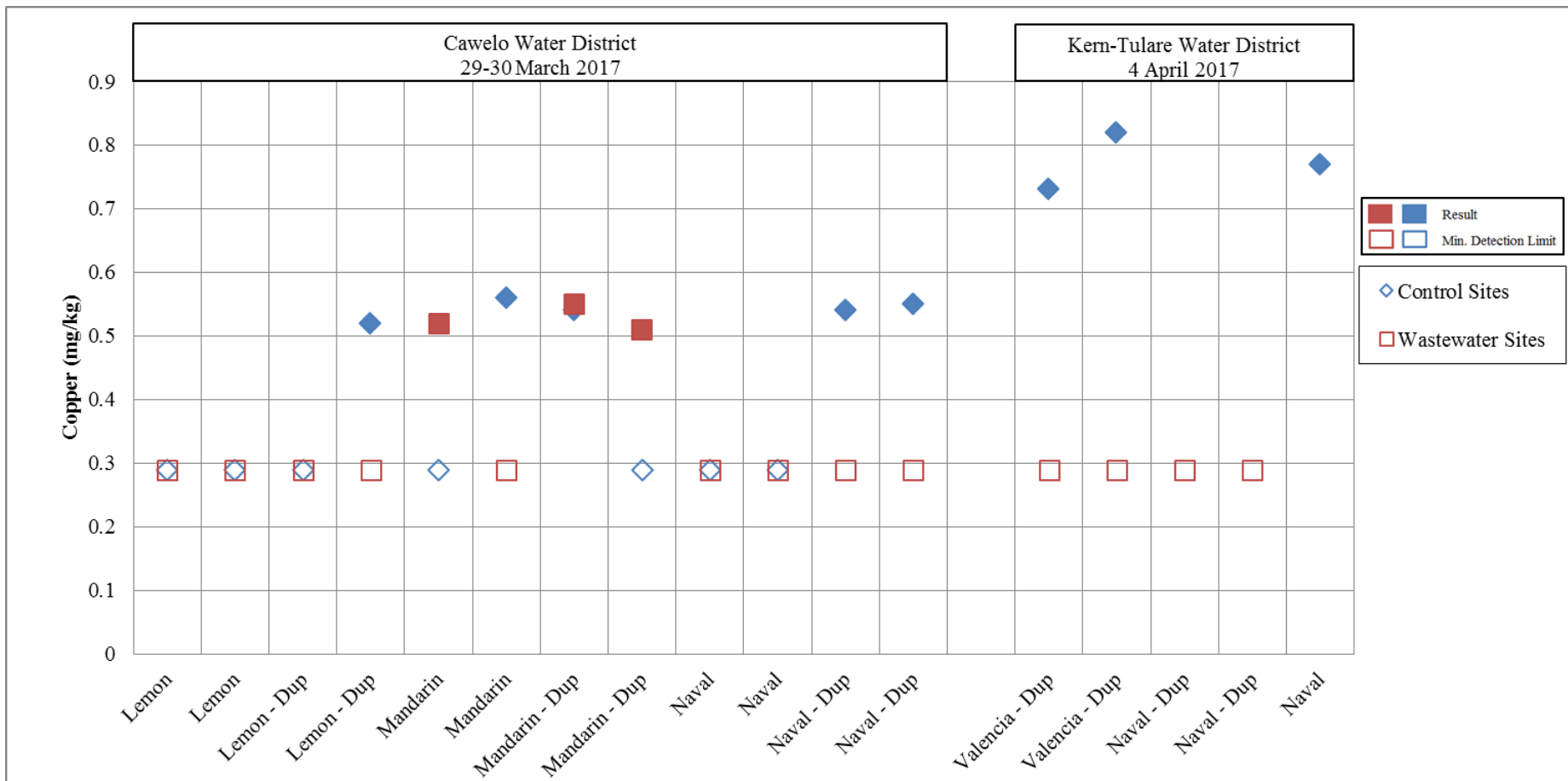
- Found in both PW irrigated & controls
- Naturally occurring in fruit (ATSDR 2007)



Copper



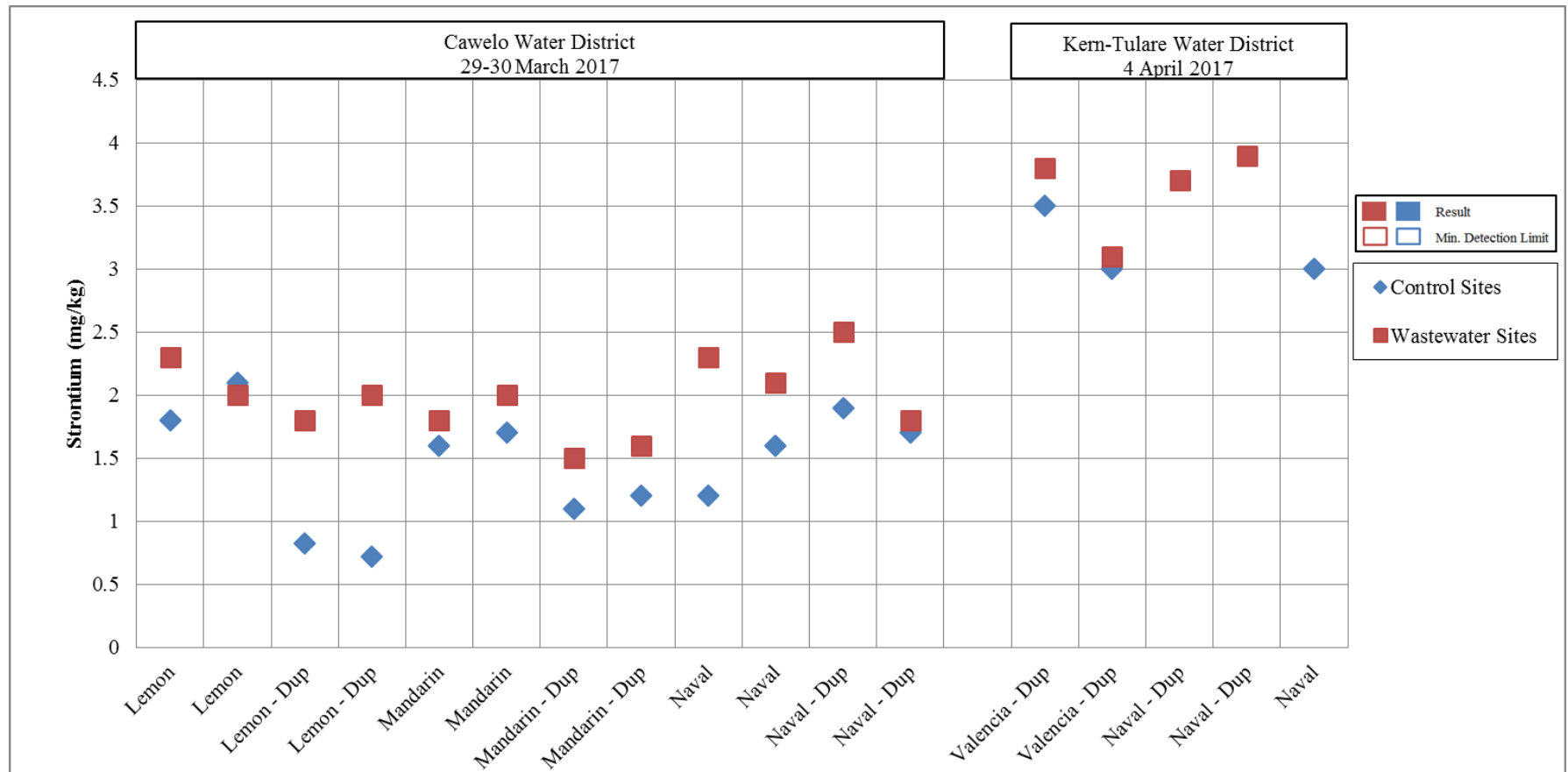
- Found in both PW irrigated & controls
- Naturally occurring in fruit (ATSDR 2004)



Strontium



- Found in both PW irrigated & controls
- Naturally occurring in fruit at mg/kg (ATSDR 2004)





Next Steps

- Write sample & analysis report
 - Interpret results in context of irrigation practices
- Plan for future studies & monitoring activities

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)



Contact information

Will Stringfellow

Wstringfellow@lbl.gov

Funding acknowledgement:

Laboratory Directed Research & Development Funds

California State Water Resources Control Board

University of the Pacific Ecological Engineering Research Program

UNIVERSITY OF THE
PACIFIC
ECOLOGICAL
ENGINEERING
RESEARCH PROGRAM



**EARTH &
ENVIRONMENTAL
SCIENCES**

