Detection of Microcystins in Water Samples from Los Angeles Area Waterbodies

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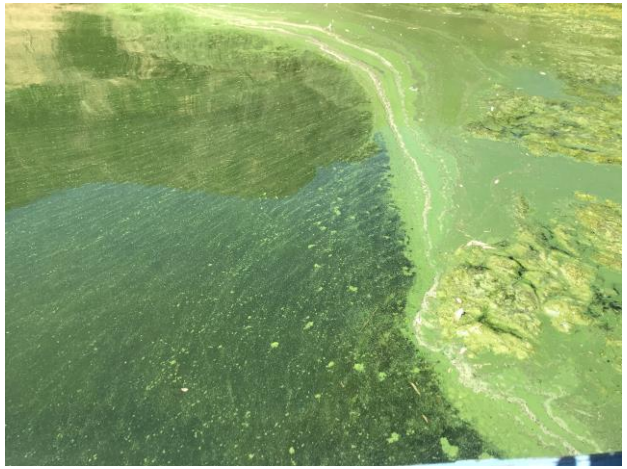
Impetus to Monitor Cyanotoxins

- **Environmental and human health concern**
- **Priority analytes in the ambient monitoring program**
- **Lack of prevalence data for better management**

Table 1: Trigger Levels For Human and Animal Health

	Caution Action Trigger	Warning TIER I	Danger TIER II
Primary Triggers			
Total Microcystins [b]	0.8 µg/L	6 µg/L	20 µg/L
Anatoxin-a	Detection [c]	20 µg/L	90 µg/L
Cylindrospermopsin	1 µg/L	4 µg/L	17 µg/L



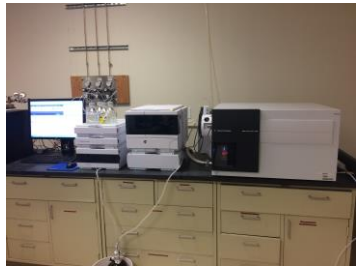
https://mywaterquality.ca.gov/habs/resources/habs_response.html

Detection Techniques to Monitor Microcystins

Enzyme-Linked ImmunoSorbent Assay (ELISA) Microcystin-ADDA

- **Measure total microcystins based on ADDA**
- **Moderately sensitive**
- **Fast and inexpensive**
- **Does not require high-end equipment and pre-concentration**

Liquid Chromatography-Tandem Mass Spectrometry (LC-MS/MS)



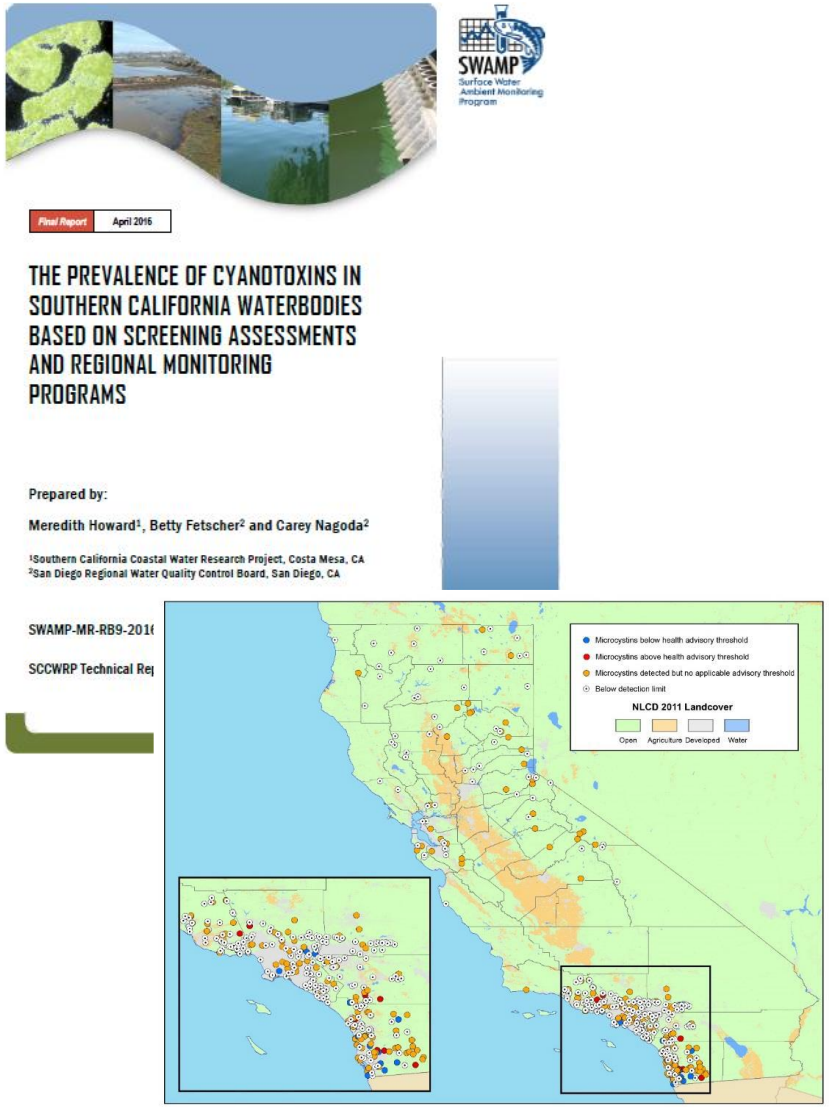
- **Measure individual microcystin variants**
- **Very sensitive and quantitative**
- **Slow and expensive**
- **Need pre-concentration and reference standards for variants**

Occurrence of Cyanotoxins in California

- **Microcystins were detectable and present in all of the waterbody types surveyed and across all land use types from <0.01 to 23.6 µg/L**

- **Multiple cyanotoxins were detected simultaneously in some systems**
  - **Microcystins**
  - **Cylindrospermopsin**
  - **Anatoxin-a**

- **Development of capacity to analyze, interpret and use passive sampling technologies in cyanotoxin monitoring.**



Study Objectives

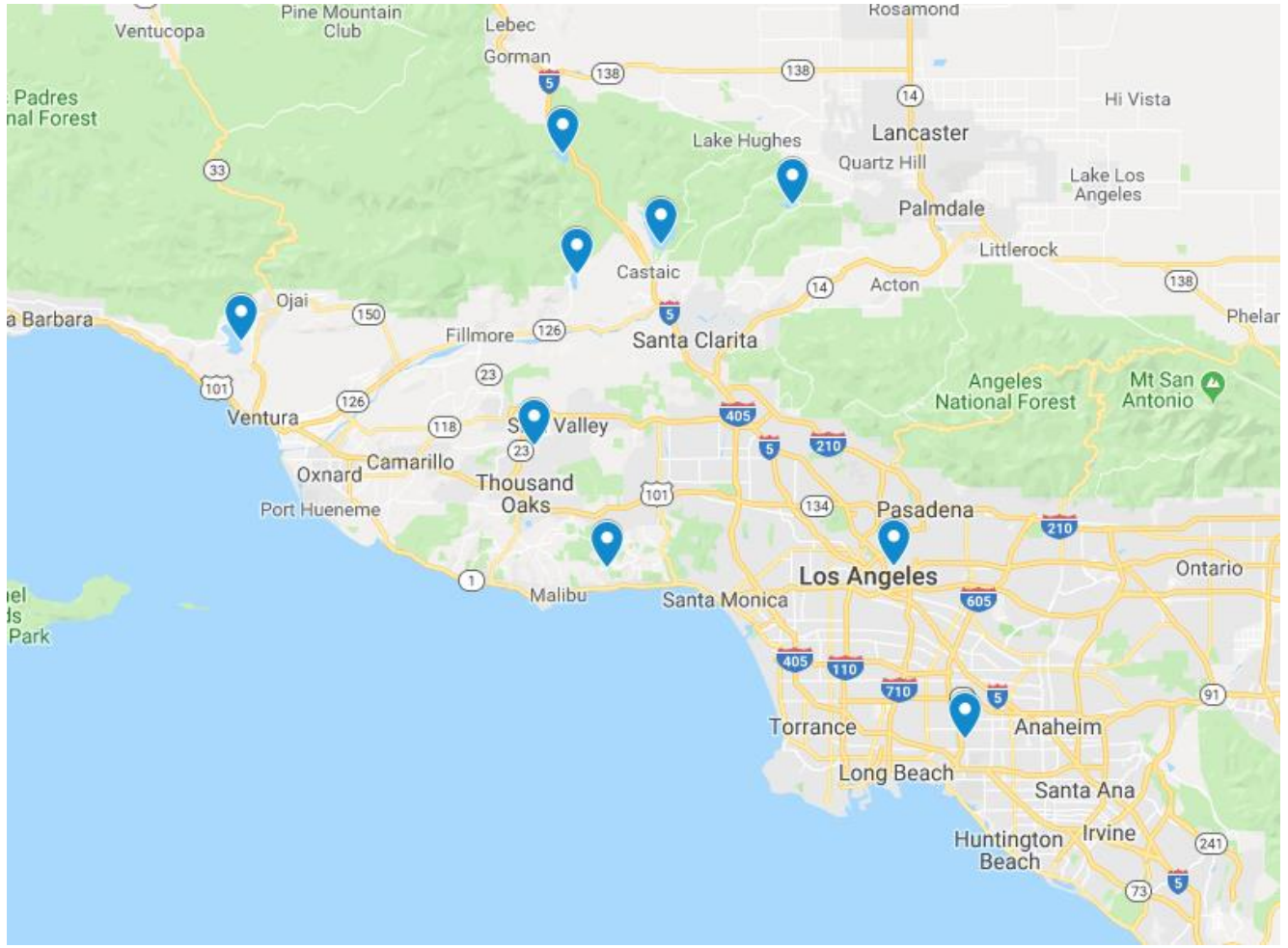
- **To provide a preliminary survey of microcystins in waterbodies across the Los Angeles region.**
- **To compare the microcystin concentrations analyzed by ELISA and LC-MS/MS**
- **To optimize passive sampling methods for extensive sampling at priority sites**

Study sites

- **Recreational and drinking water reservoirs**

- **City park lakes**

    1. **Pyramid Lake**
    2. **Lake Piru**
    3. **Lake Casitas**
    4. **Castaic Lake**
    5. **El Dorado Park**
    6. **Lincoln Park**
    7. **Malibu Creek**
    8. **Bard/Wood Ranch Res**
    9. **Bouquet Reservoir**



Sampling

- One-time grab samples
- Two locations per site
- Water samples collected in Sep-Nov 2018
- Sediment collected if available

Analytical Methods

ELISA (USEPA 546 and Ohio EPA 701.0)

Detection limits

10 mL water → Lysing by Freeze-Thaw (3 cycles) → ELISA analysis of total microcystins

0.1 µg/L

LC-MS/MS (derive from USEPA 544)

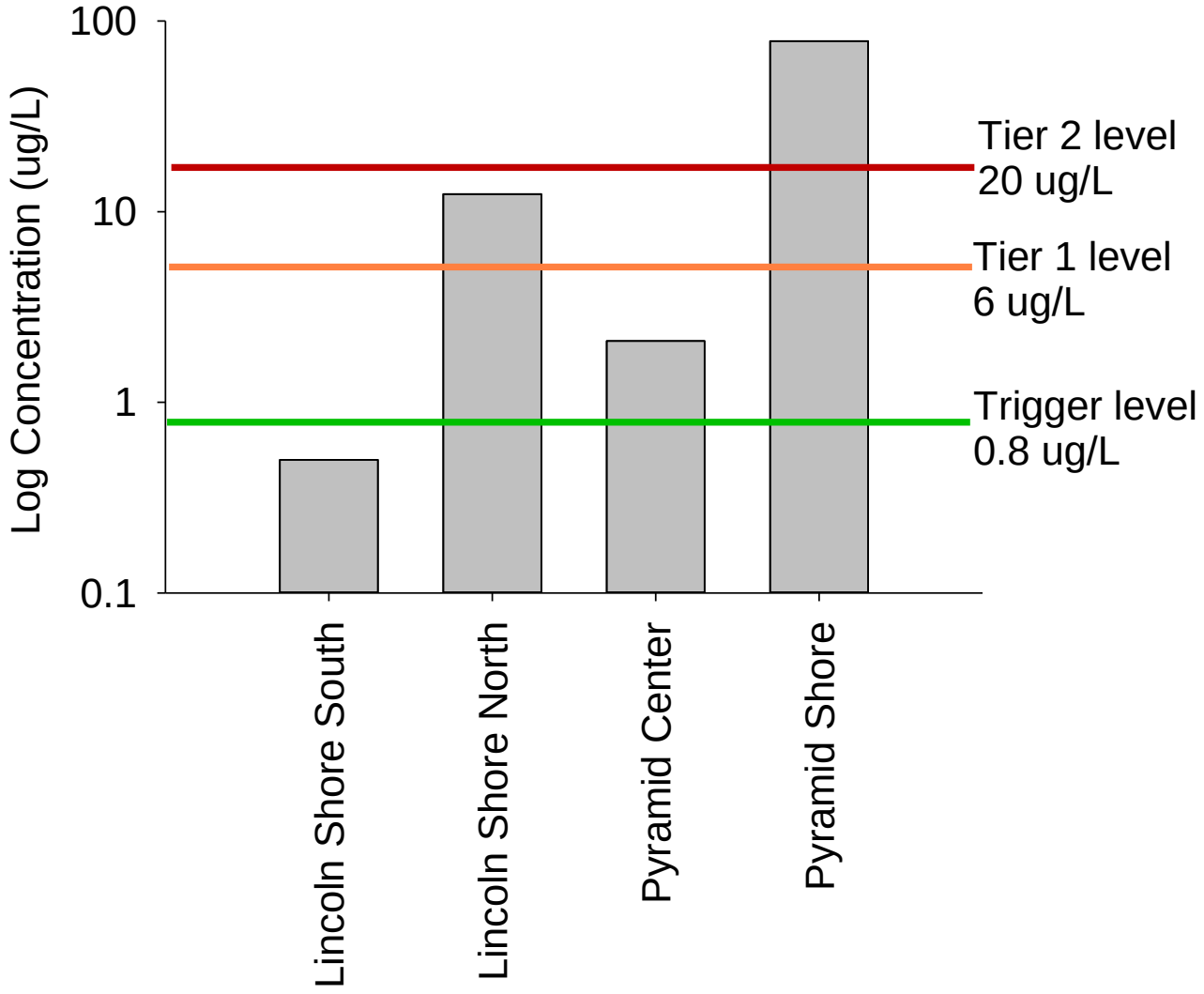
500 mL water → Solid Phase Extraction → LC-MS/MS analysis of individual microcystins and nodularin

0.002-0.05 µg/L estimated

Individual microcystins (MC): MC-LR, MC-YR, MC-RR, MC-LY, MC-LA, LC-LW, MC-LF, MC-WR, MC-HilR, desmethyl-MC-LR, and desmethyl-MC-RR.

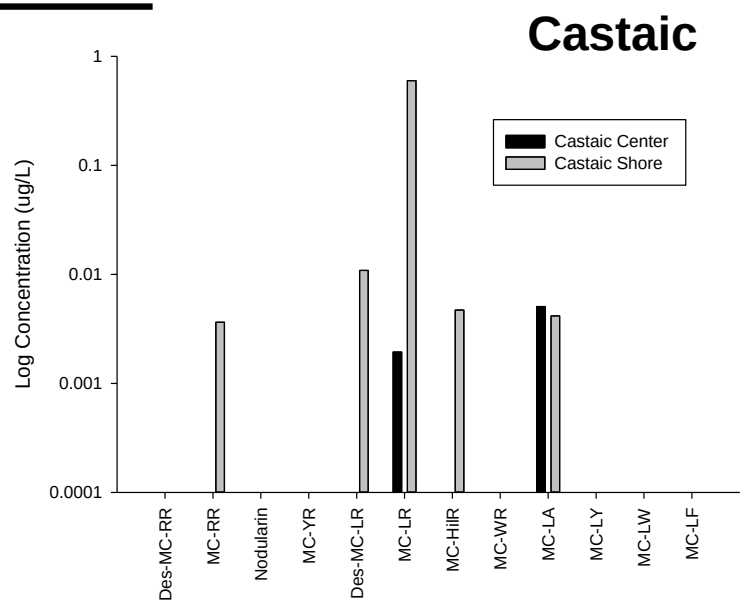
ELISA Result

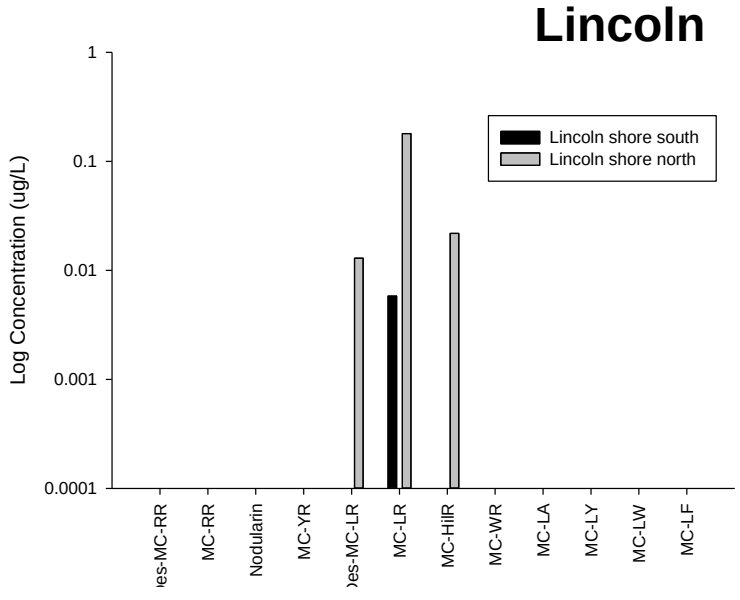
- **Microcystins detected in 7 of 9 waterbodies with 5 sites below trigger level**
- **Microcystins detected above Tier 1 in Lincoln Park Lake and Pyramid Lake**
- **Higher concentration detected at windward locations**

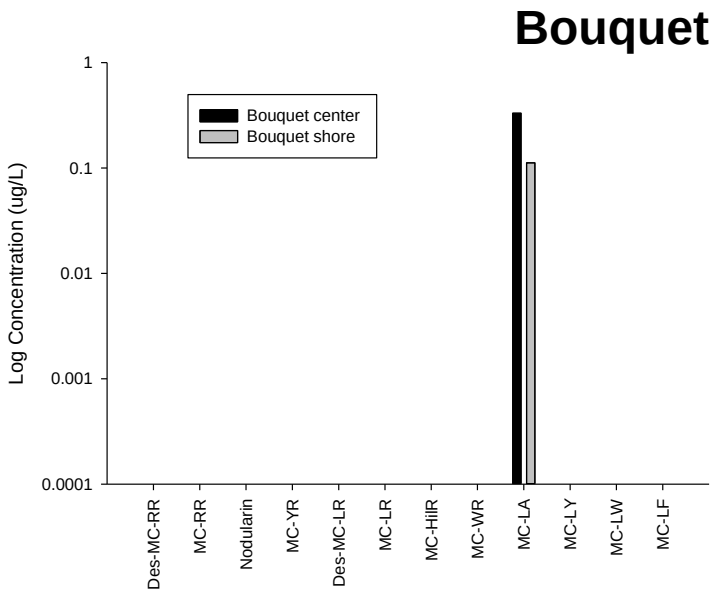


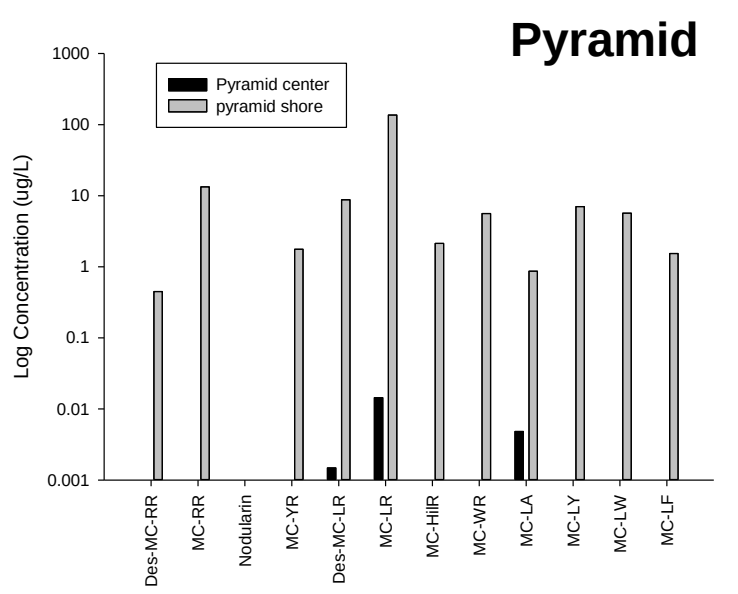
LC-MS/MS Result

- **Microcystins were detected in 4 of 7 waterbodies that were detected by ELISA**
- **MC-LR was the dominant microcystin variant**
- **All MC compounds were detected in Pyramid Lake shore**









Method comparison

- **Lower total MCs by LC-MS/MS in 9 samples**
- **Both methods were ND in in 5 samples**
- **Differences between ELISA and LC-MS/MS was sometimes large (90-fold)**
  - **Not all variants captured by LC-MS/MS**
- **ELISA is semi-quantitative at best**

Site	ELISA (µg/L)	LC-MS/MS (µg/L)	RPD%
Bard Center	0.21	ND	
Bard Shore	ND	ND	
Bouquet Center	0.17	0.33	64
Bouquet Shore	ND	0.11	
Casitas Center	0.63	<0.002	199
Casitas Shore	0.17	<0.002	195
Castaic Center	0.21	0.007	187
Castaic Shore	0.15	0.62	122
El Dorado North	ND	ND	
El Dorado South	ND	ND	
Lincoln Shore North	12	0.21	193
Lincoln Shore South	0.50	0.006	195
Malibu Creek Down	ND	ND	
Malibu Creek Up	ND	ND	
Piru Center	0.14	ND	
Piru shore	0.16	ND	
Pyramid Center	2.1	0.74	96
Pyramid Shore	78	184	81

Summary

- **Microcystins were detected at 7 sites (0.14-78 µg/L) by ELISA and detected at 4 sites (<0.002-184 µg/L) by LC-MS/MS.**
- **The agreement between ELISA and LC-MS/MS was variable, with ELISA results higher in 9 samples (vs 4 for LC-MS/MS), and differences as high as 90-fold**
- **A prioritized list of LA area waterbodies for future more intensive monitoring includes Pyramid and Lincoln Park Lakes**
- **Further efforts are planned to validate and expand LC-MS/MS methods for microcystins as well as other cyanotoxins**

Acknowledgements

- California State Water Resources Control Board

- Staffs at agencies that oversee the waterbodies
  - City of Long Beach
  - City of Los Angeles, Department of Recreation and Parks
  - Calleguas Municipal Water District
  - Los Angeles Department of Water and Power
  - United Water Conservation District
  - California Department of Parks and Recreation

Thank you!

Questions?