Tools for Field Monitoring: Solid Phase Adsorption Toxin Tracking (SPATT) and a few other methods

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LIMNOLOGY
and
OCEANOGRAPHY: METHODS

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Application of Solid Phase Adsorption Toxin Tracking (SPATT) for field detection of the hydrophilic phycotoxins domoic acid and saxitoxin in coastal California

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Solid Phase Adsorption Toxin Tracking

"A simple and sensitive *in situ* (monitoring) method… involves the passive adsorption of biotoxins onto porous synthetic resin filled sachets (SPATT bags) and their subsequent extraction and analysis."

MacKenzie et al. (2004) Toxicon

A brief history of SPATT

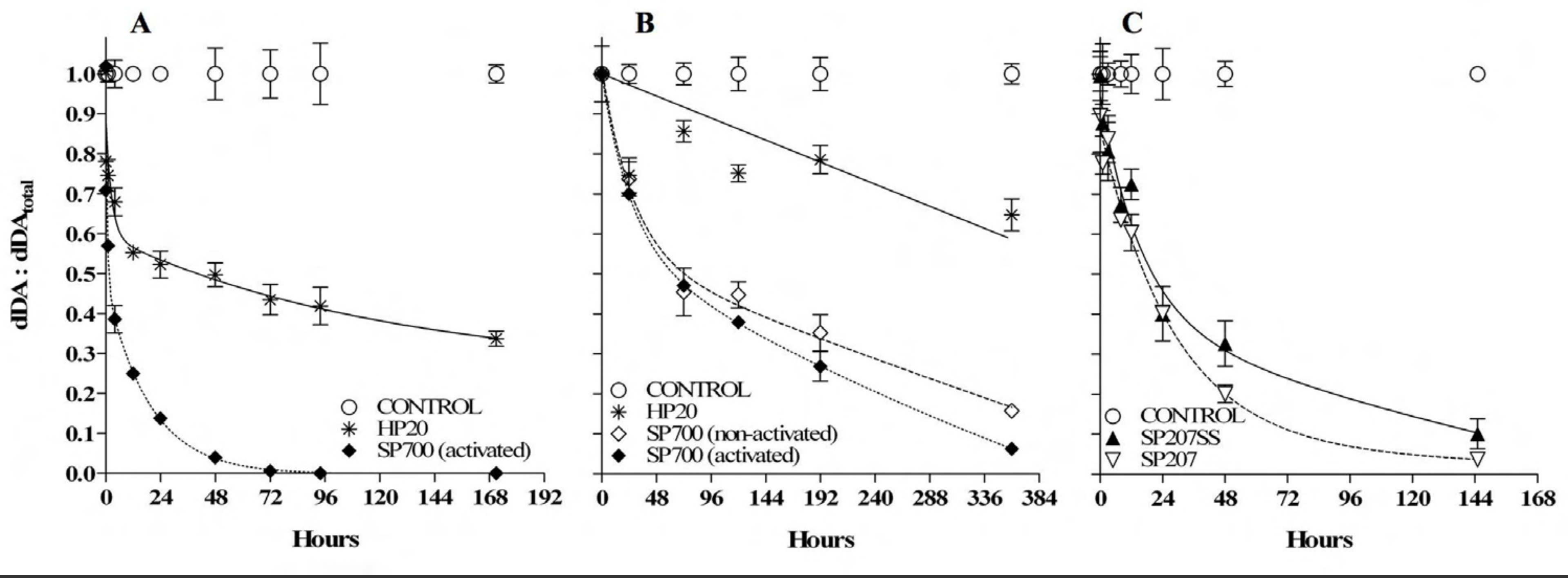
From lipophilics to hydrophilics

Table 1. Published studies on the employment of Solid Phase Adsorption Toxin Tracking (SPATT). Phycotoxin abbreviations are as follows: dinophysistoxin (DTX), okadaic acid (OA), pectenotoxin (PTX), yessotoxin, (YTX), gymnodimine (GD), azaspiracid (AZA), spirolide (SPX), domoic acid (DA), saxitoxin, and related paralytic shellfish toxins (PST). Bold text indicates the resin identified as optimal for the toxins addressed in the study.

Study	Toxin group analyte	Resins	Region	Mode of deployment
MacKenzie et al. (2004)	DTX, OA, PTX, YTX	**HP20**, SP207, HP2MG	New Zealand	Sewn bags
Takahashi et al. (2007)	GD, OA, PTX	HP20	Australia	Sewn bags
Rundberget et al. (2007)	DTX, OA, PTX	HP20	Norway, Spain	Packed columns
Turrell et al. (2007)	OA, PTX, YTX, AZA	HP20, **SP700**	Ireland	Zip-tied mesh bags
Turrell et al. (pers. comm.)	DA	HP20, **SP700**	Ireland	Zip-tied mesh bags
Pizarro et al. (2008a, 2008b)	DTX, OA, PTX	HP20	Spain	PVC frame
Fux et al. (2008)	DTX, OA	**HP20**, SP850, SP825L, XAD4, L-493	Ireland	Sewn bags, Embroidery disc
Fux et al. (2009)	DTX, OA, PTX, YTX, AZA, SPX	HP20	Ireland	Embroidery disc
Rundberget et al. (2009)	OA, PTX, YTX, AZA, SPX	HP20	Norway	Embroidery disc
This study	DA, PST	HP20, SP700, SP207, SP207SS	USA (California)	Heat-sealed bags

Lane et al. (2010) L&O Methods

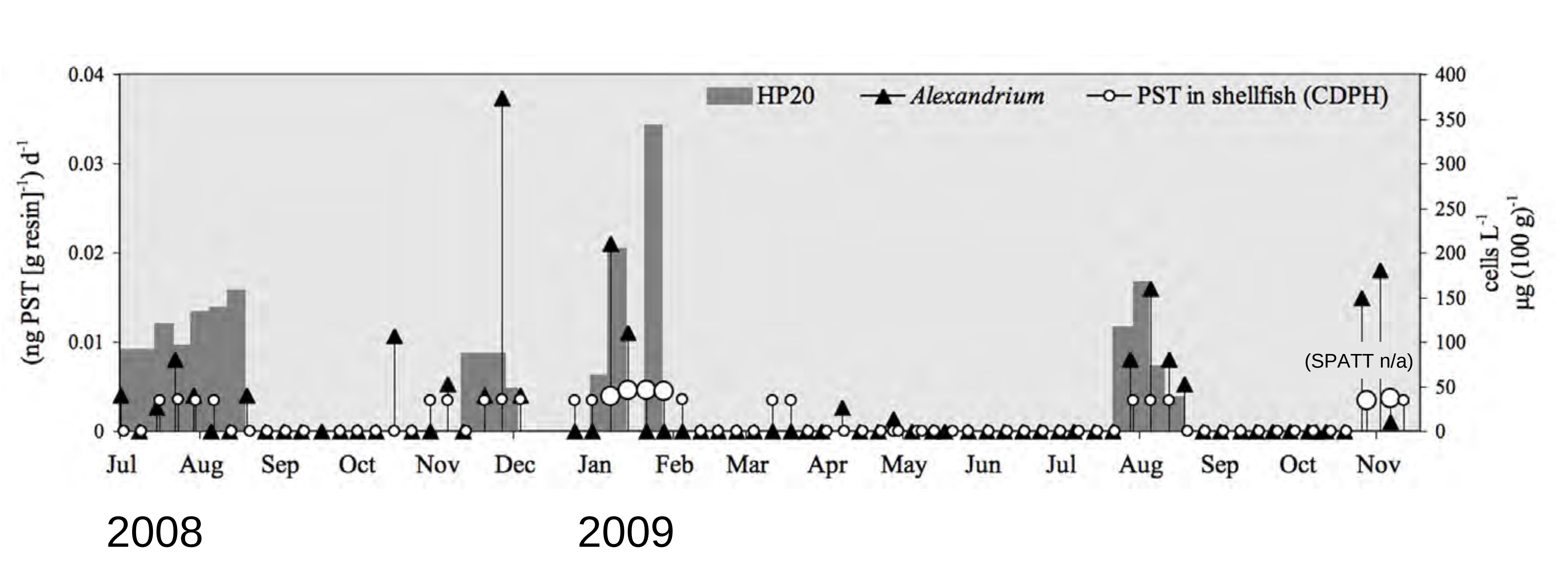
Resin selection



Lane et al. (2010) L&O Methods

STX-SPATT at SC Wharf

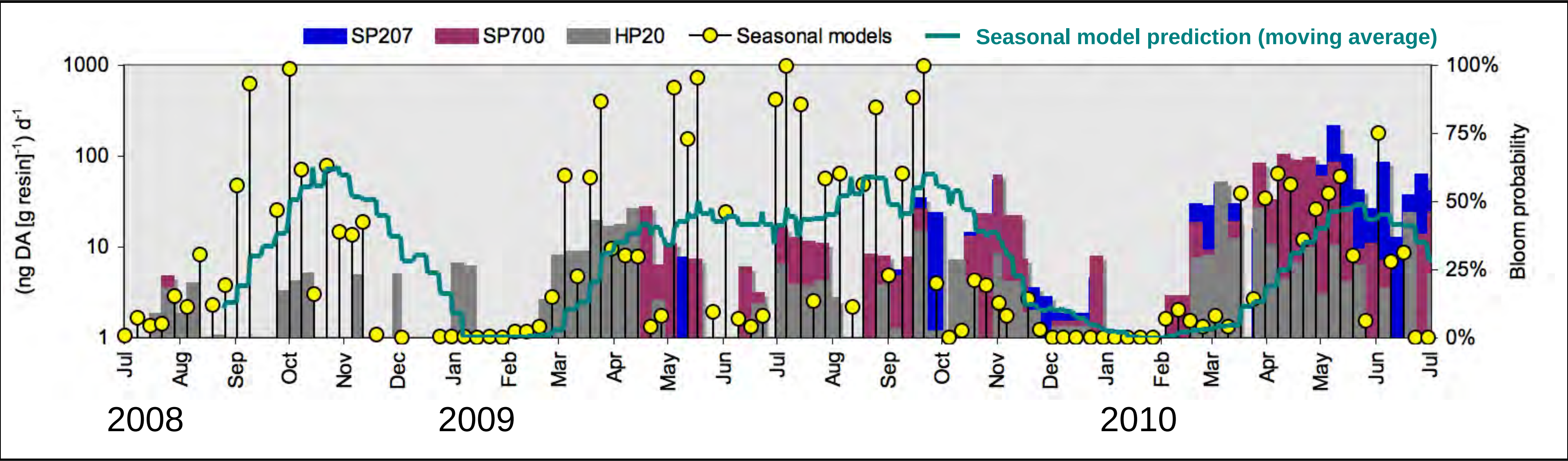
-Concurrent detection of DA/STX



Lane et al. (2010) L&O Methods

New insight from… # Integrative monitoring tools:

SPATT + predictive models

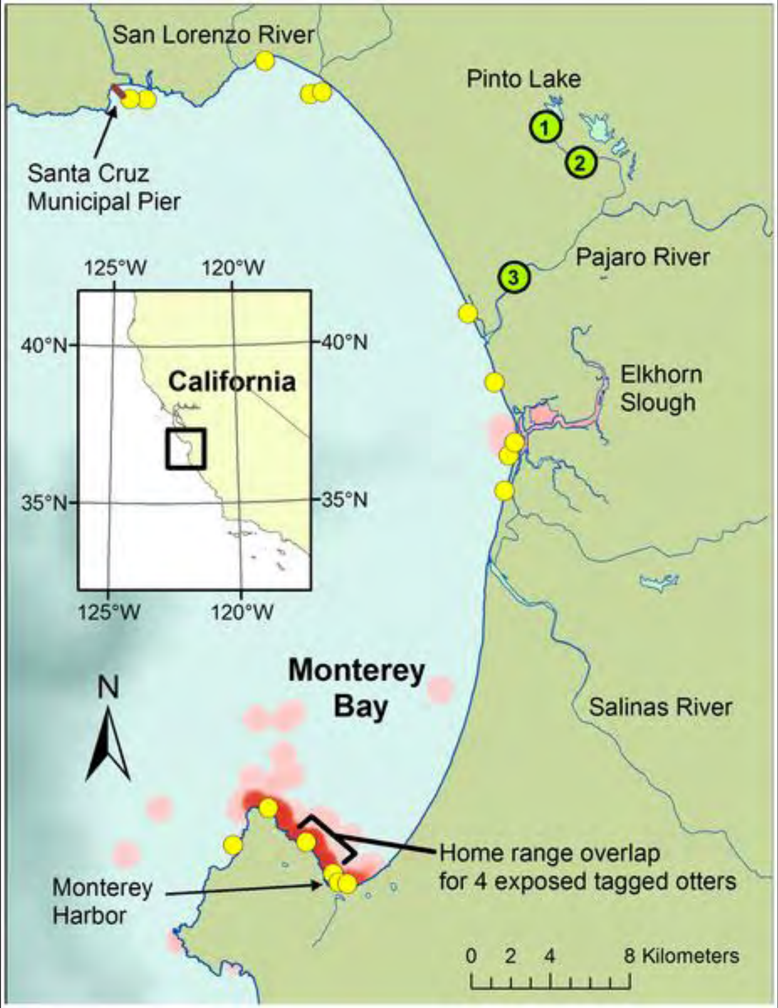


As an integrative sampler, SPATT monitors domoic acid through time (across a week, as deployed at SCMW).

Developed from regional data to describe environmental patterns, predictive bloom models resolve broad spatial dynamics.

Discrete model predictions and SPATT data match very closely;
the two technologies simultaneously signal bloom conditions (models) and toxin incidence (SPATT) which are otherwise unrecognized and/or unanticipated by RAI, cell counts, etc.

MC-SPATT



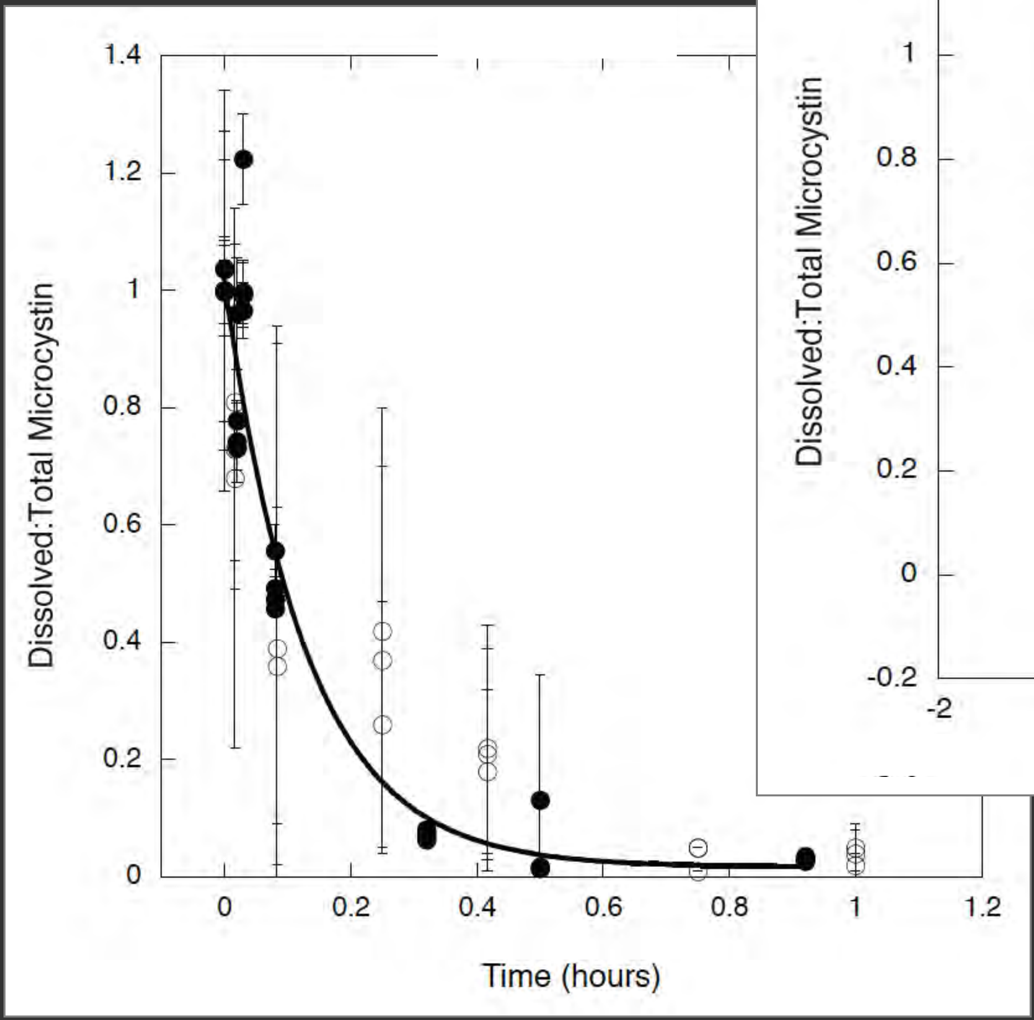
Miller et al. PLOS ONE 2010

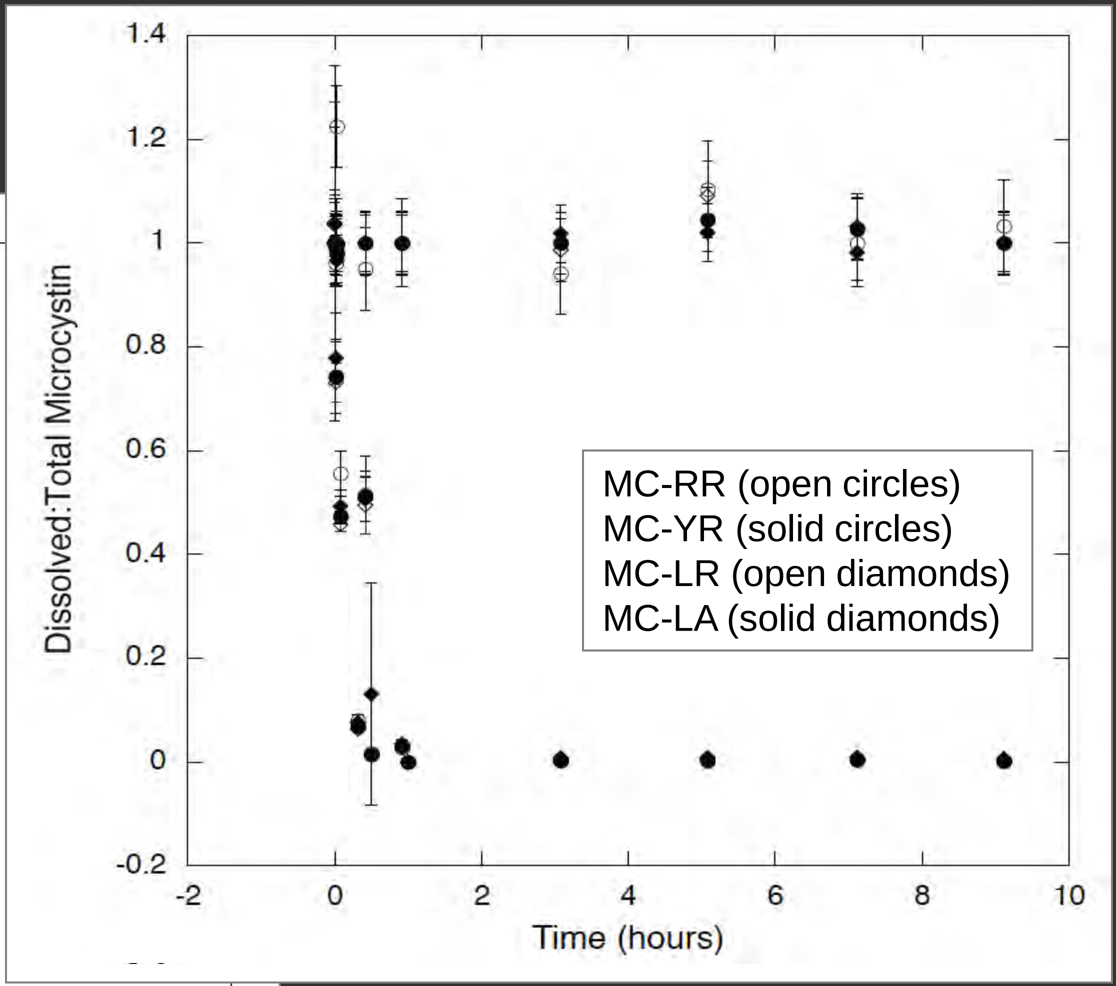
Why use SPATT?

- It is time-integrative and has a very low limit of detection
- Can be placed in fresh, brackish, or saltwater
- Amenable to multiple toxin detection methods, can be archived for analysis of other toxins

MC-SPATT

- Application of SPATT with microcystin

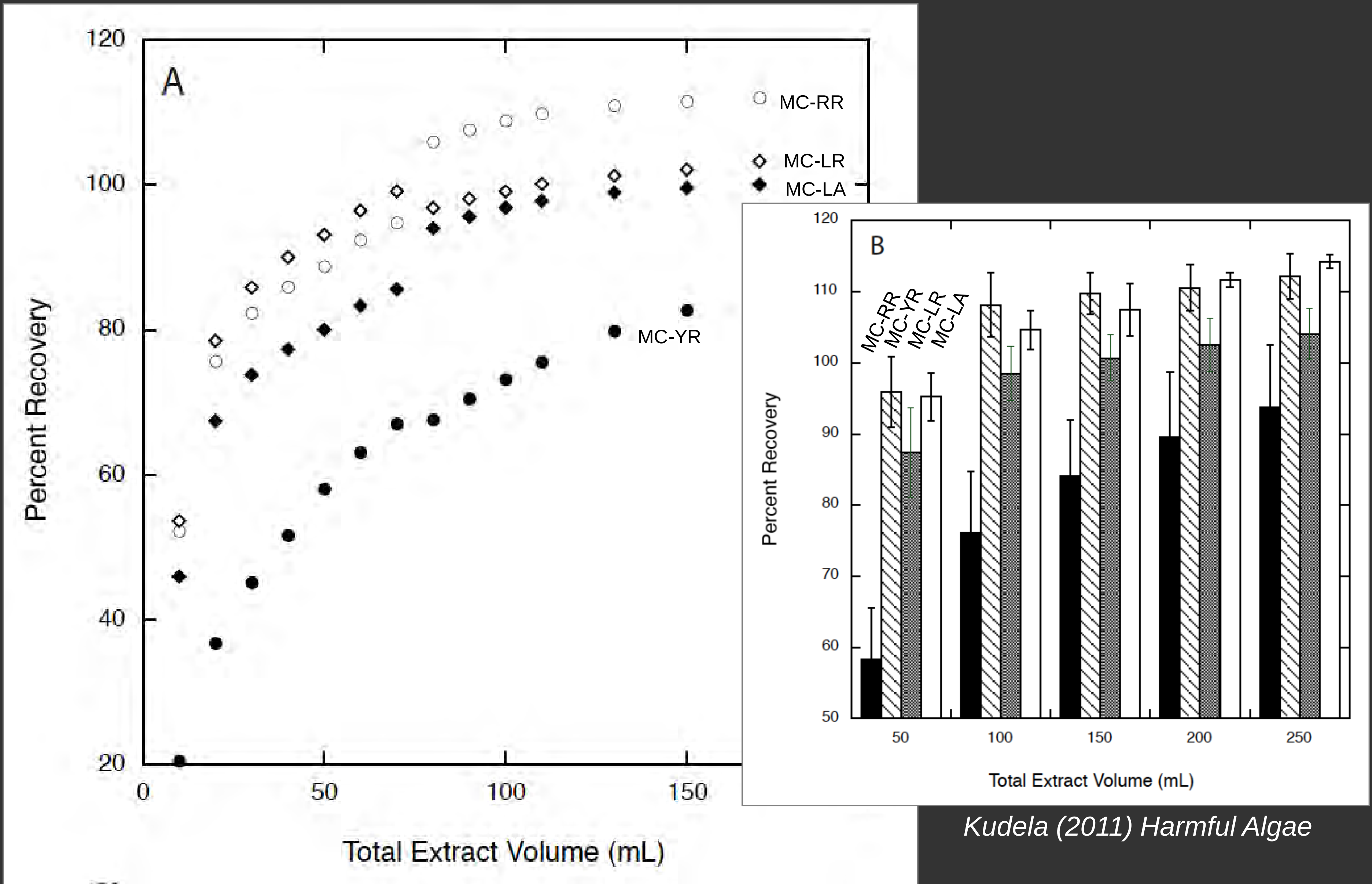




Kudela (2011) Harmful Algae

MC-SPATT

- Application of SPATT with microcystin



Kudela (2011) Harmful Algae

MC-SPATT

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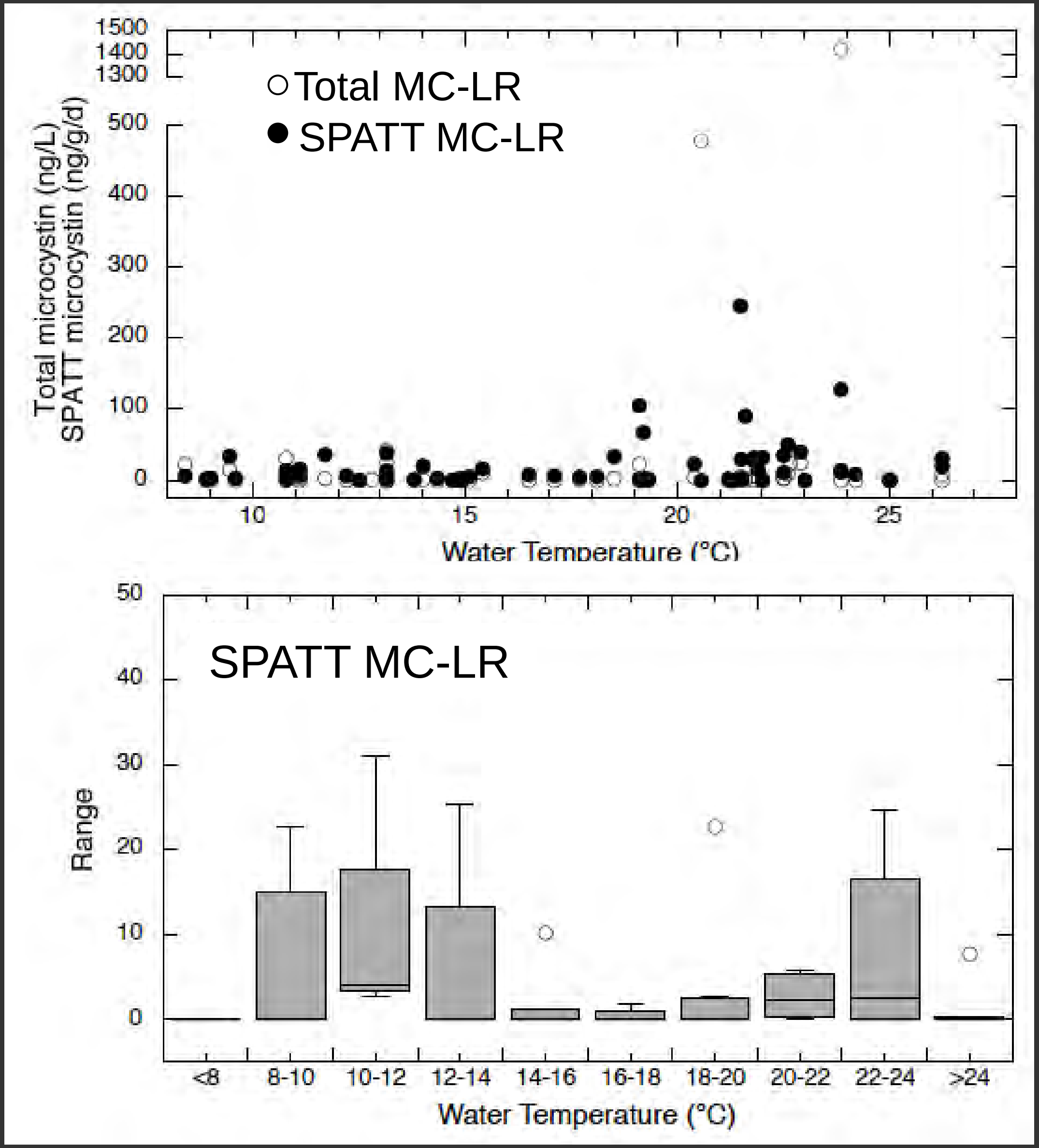


Kudela (2011)
Harmful Algae

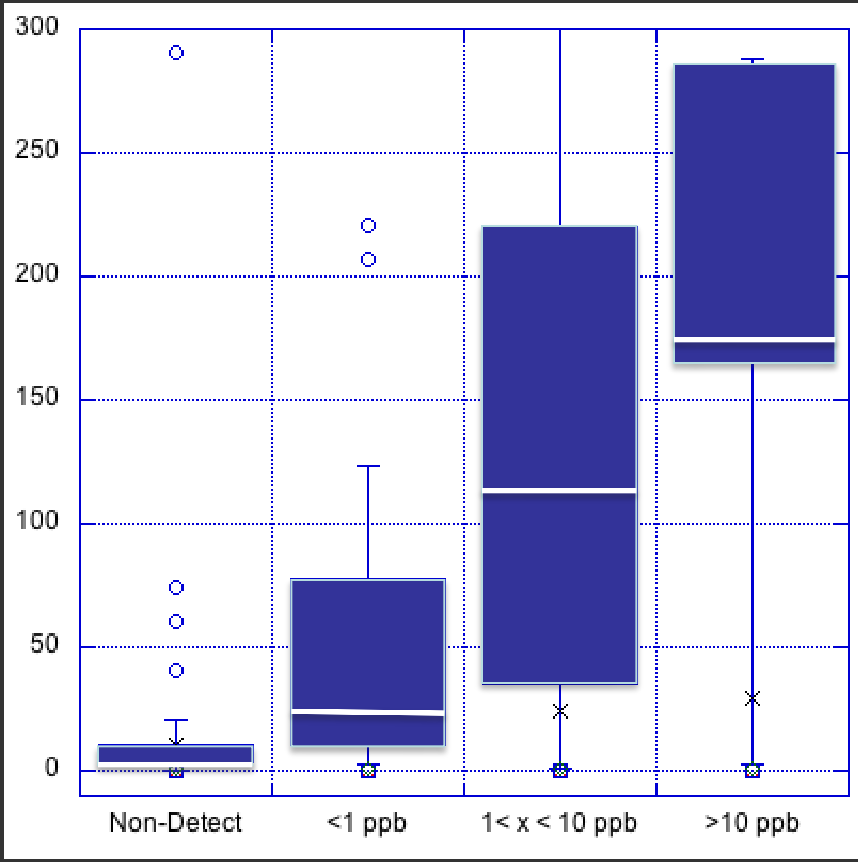
Why NOT use SPATT?

Values are reported as mass (ng) toxin per gram resin deployed, for some period of time. Difficult to directly compare to regulatory limits, which are typically based on grab samples or on contamination of food products.

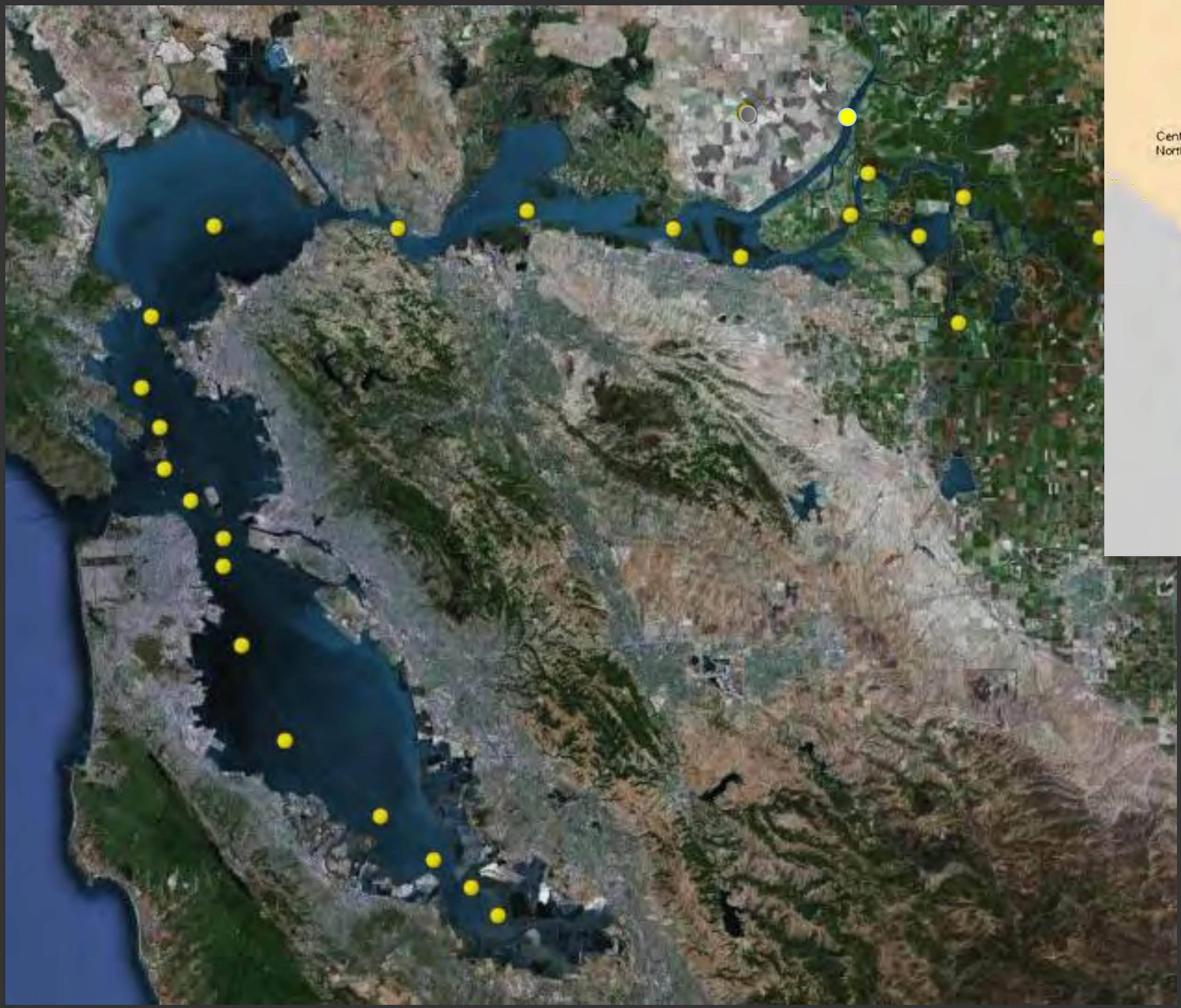
Grab vs. SPATT (7 day deployments*)

Grab Sample (ppb)	SPATT (ng/g)
Non-Detect	5-13
< 1 ppb	20-50
1< x < 10 ppb	100-200
> 10 ppb	175-245

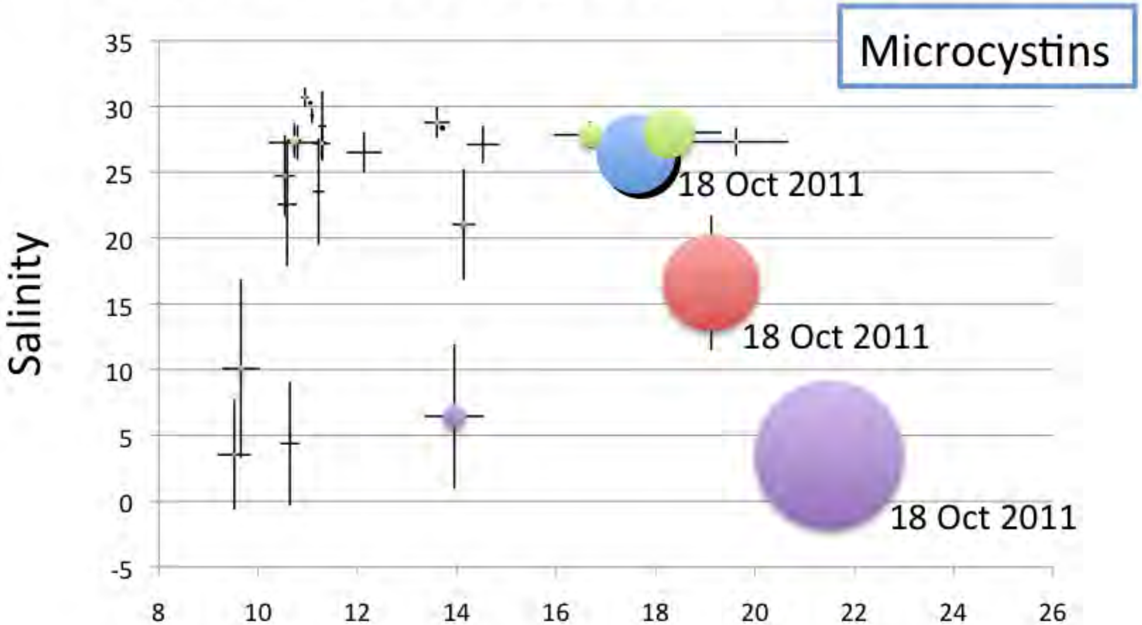
*No statistical difference between 5-30 days

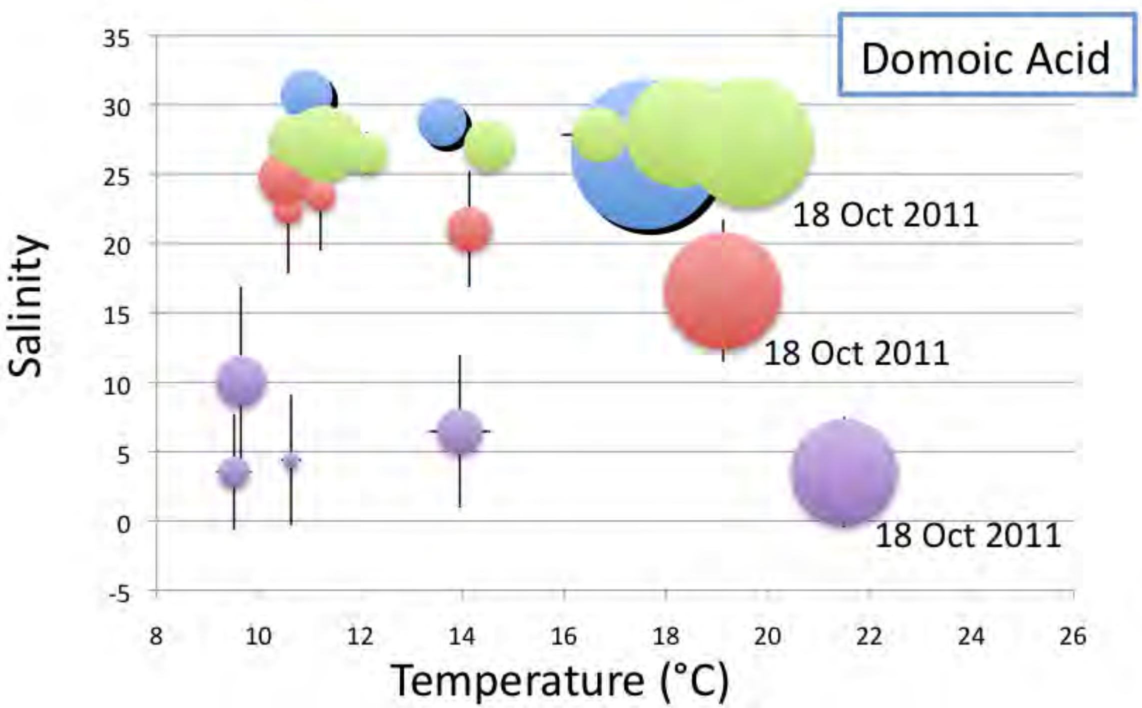


2011-2012: USGS Deployment of SPATT



SPATT concentrations plotted in Temperature-Salinity space





Bubble size = toxin concentration; color corresponds to Bay regions

Bars represent 1 SD for Salinity and Temperature

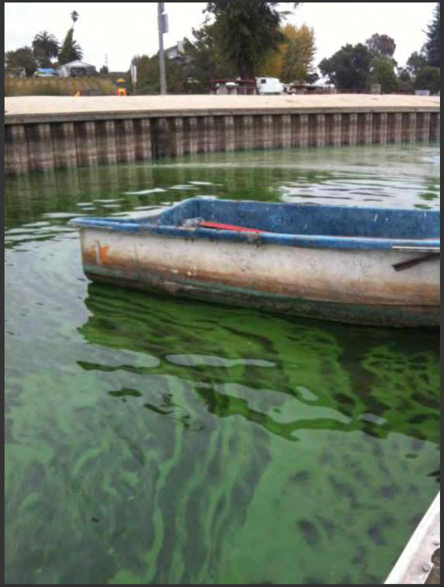
Environmental Drivers of Toxin Production: Pinto Lake

Relative Importance

More

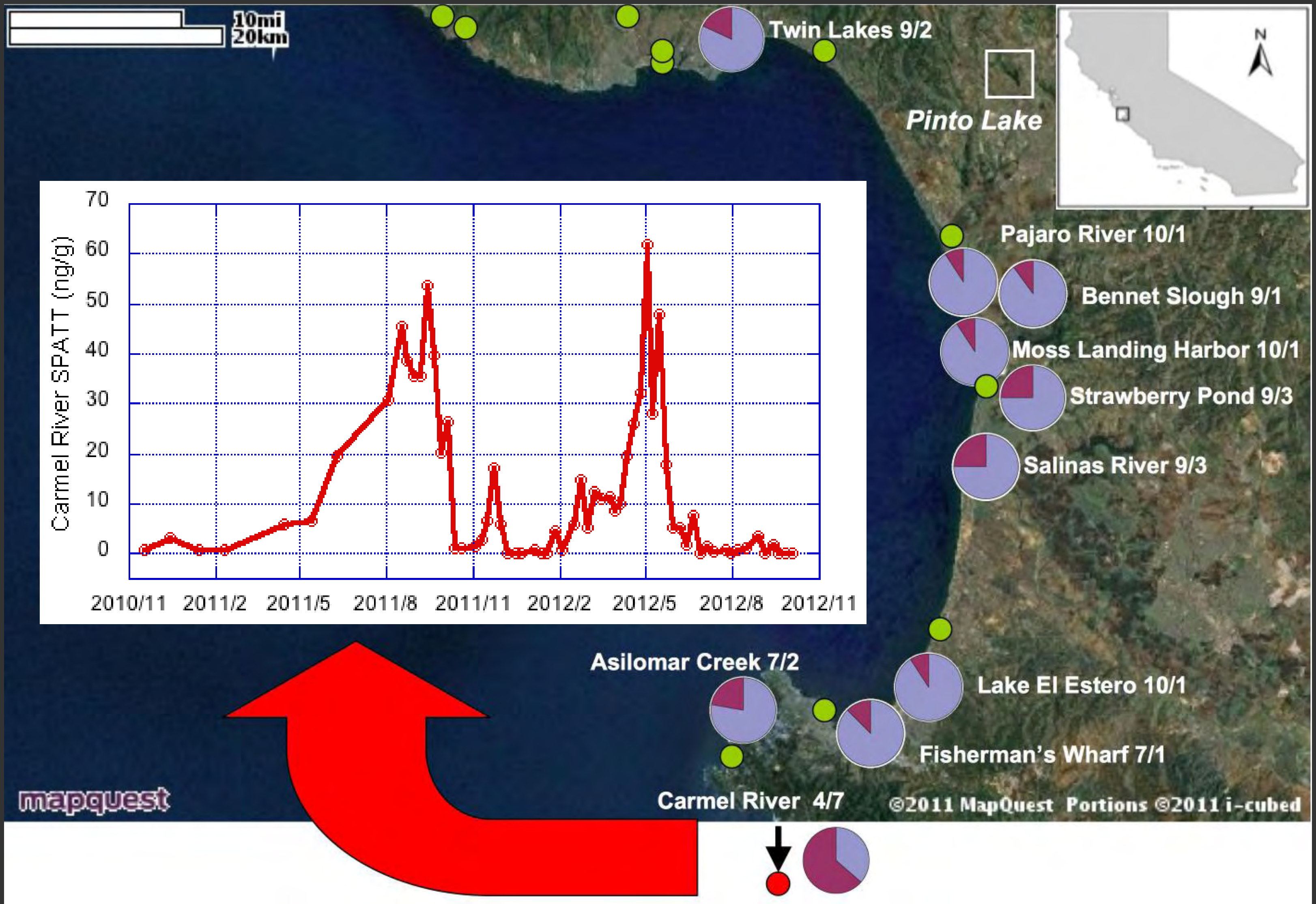
Less

2009-2010 (N=66)	Canonical Correlation, 1st Axis
Phosphate	-0.443 (p=0.17)
Chlorophyll	0.141 (0.03)
TDN	-0.390 (0.05)
Water Temperature	0.124 (0.27)
NPOC	-0.312 (0.62)
Si:N Ratio	-0.133 (0.34)
Silicate	-0.313 (0.38)
N:P Ratio	-0.382 (0.19)



Kudela, Harmful Algae 2011

Monterey Bay Toxins (2010-11, monthly sampling)



Environmental Drivers of Toxin Production: Monterey Bay

2010-2012 (N=164)

Principal Components regression (rotated loadings)

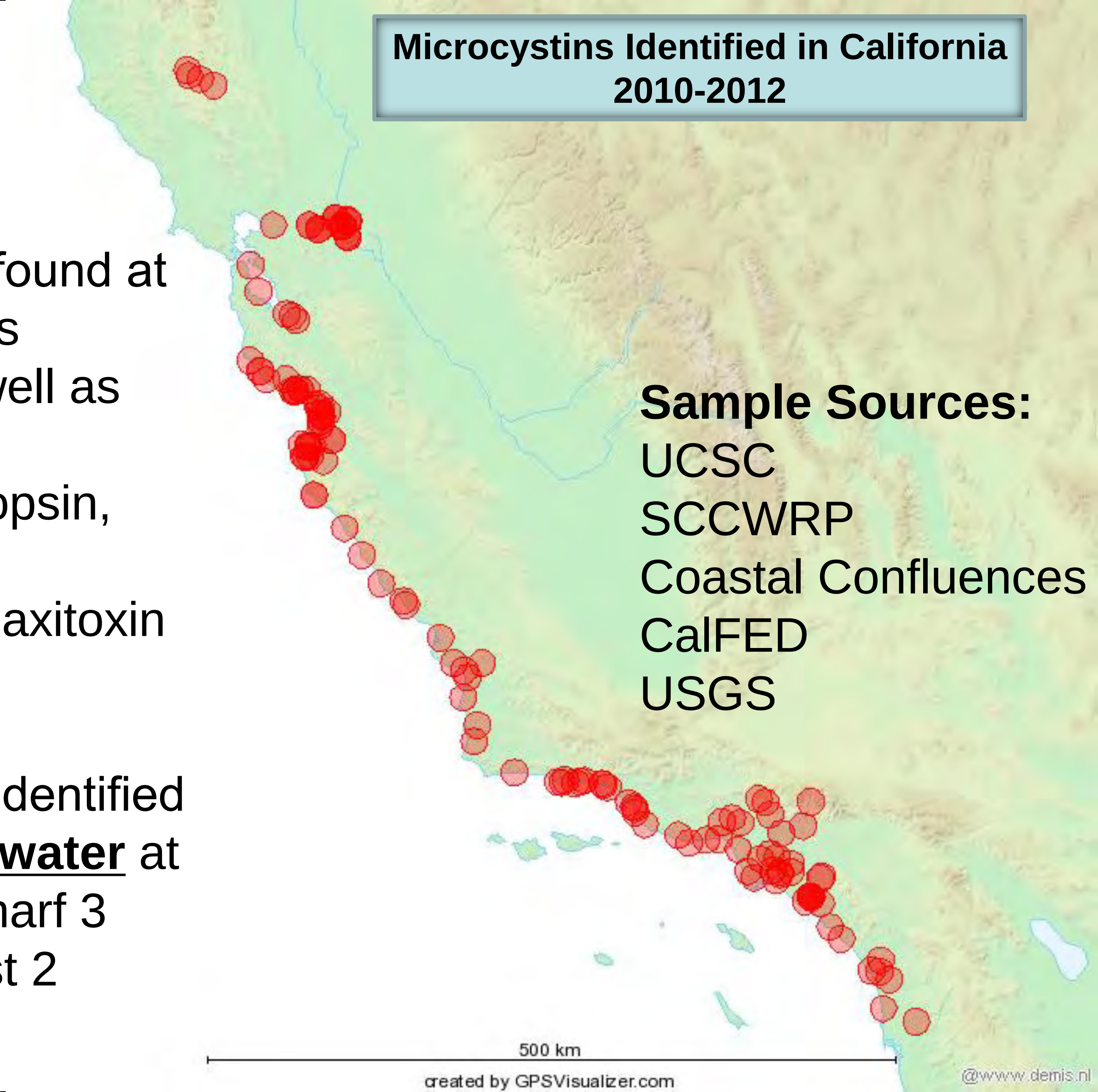
Variable	PC	Loading	Interpretation
Date	**PC1**	0.902	*Seasonality*
Temperature		0.892	
Ammonium	**PC2**	0.857	*Anthropogenic Nutrient Loading*
Urea		0.846	
Nitrate	**PC3**	0.832	*Nutrient Loading and river flow?*
Phosphate		0.646	
Silicate		-0.613	

Microcystins Identified in California 2010-2012

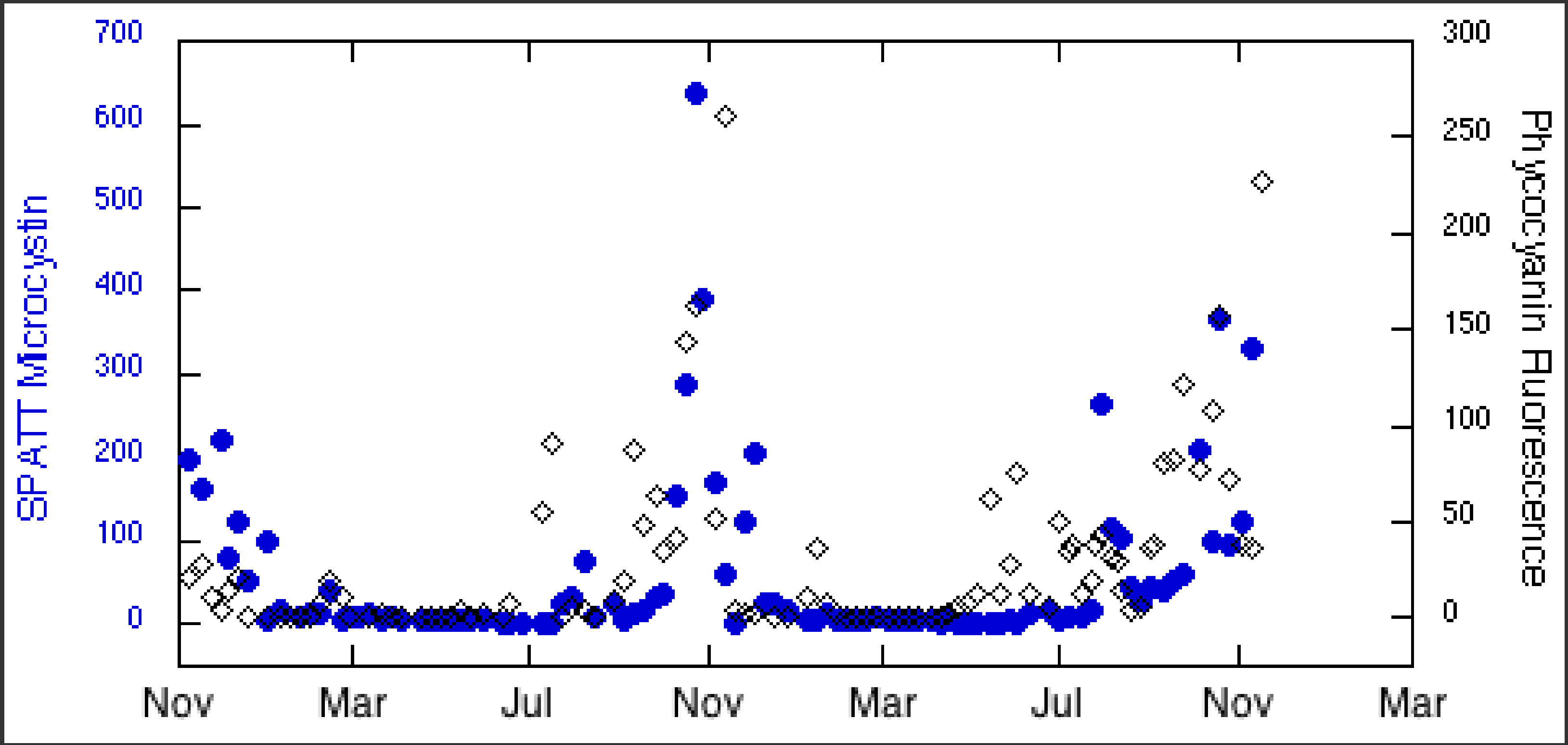
- Microcystins found at 116 of 157 sites surveyed (as well as low levels of cylindrospermopsin, anatoxin-a, lyngbyatoxin, saxitoxin at some sites)

- Microcystins identified in **<u>full salinity water</u>** at Santa Cruz Wharf 3 times in the last 2 years

Sample Sources:
UCSC
SCCWRP
Coastal Confluences
CalFED
USGS



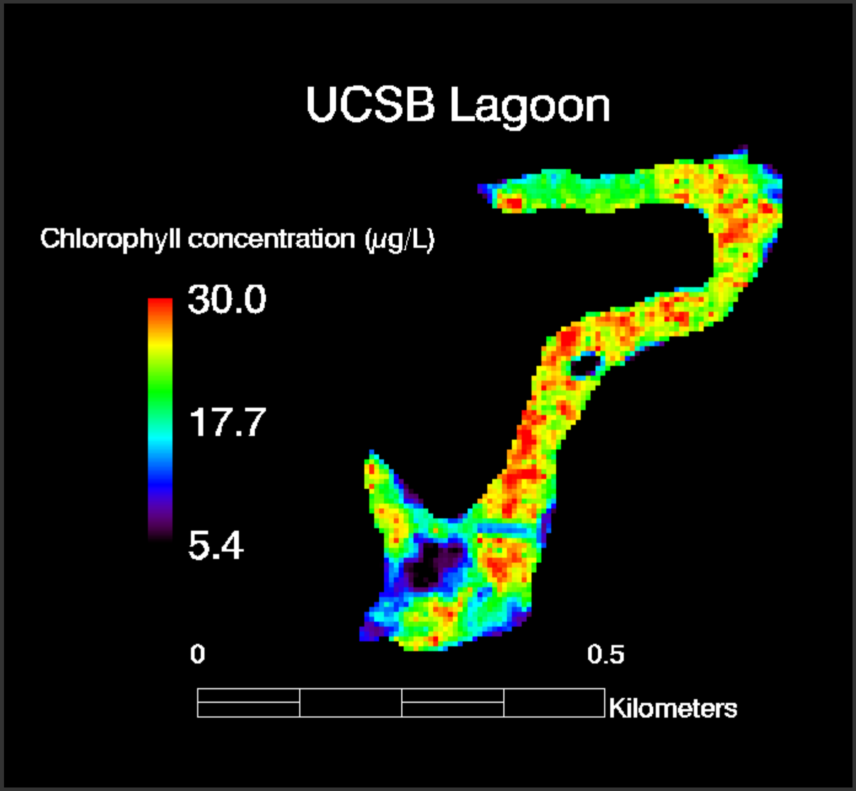
Other Monitoring Tools

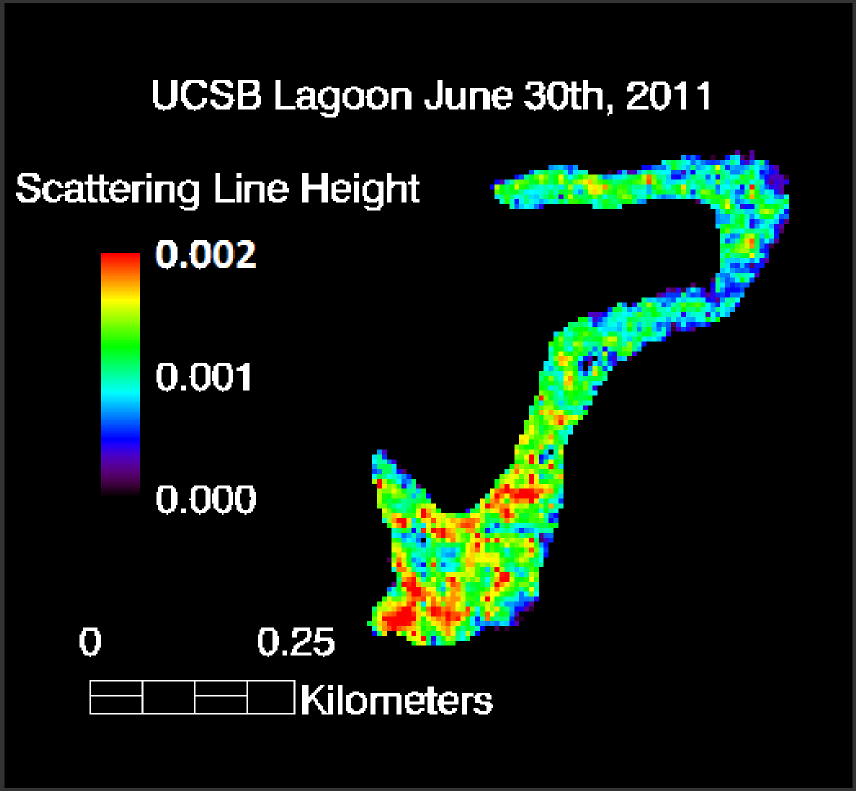


Pinto Lake weekly time-series, 2011-2012

Santa Barbara MASTER 2011 MSLH

- MSLH=MASTER Scattering Line Height (spectral shape—identifies cyanos)

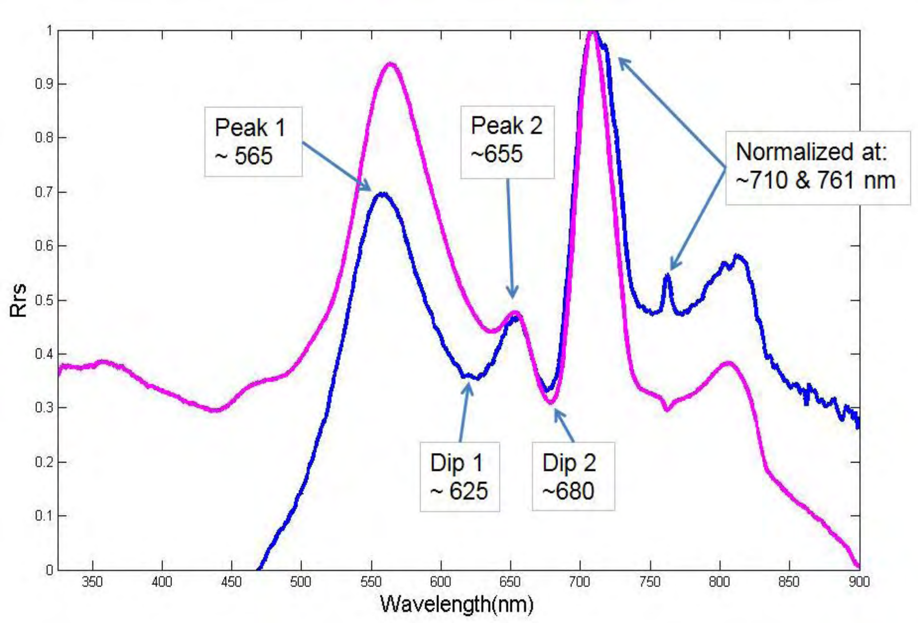


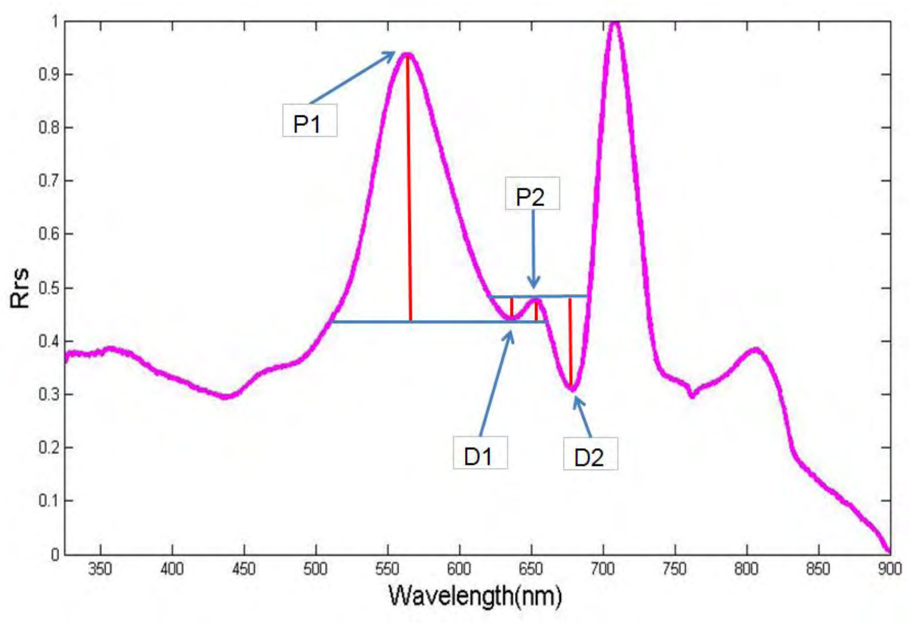


Spectral Shape Indices for *Aphanizomenon* versus *Microcystis*

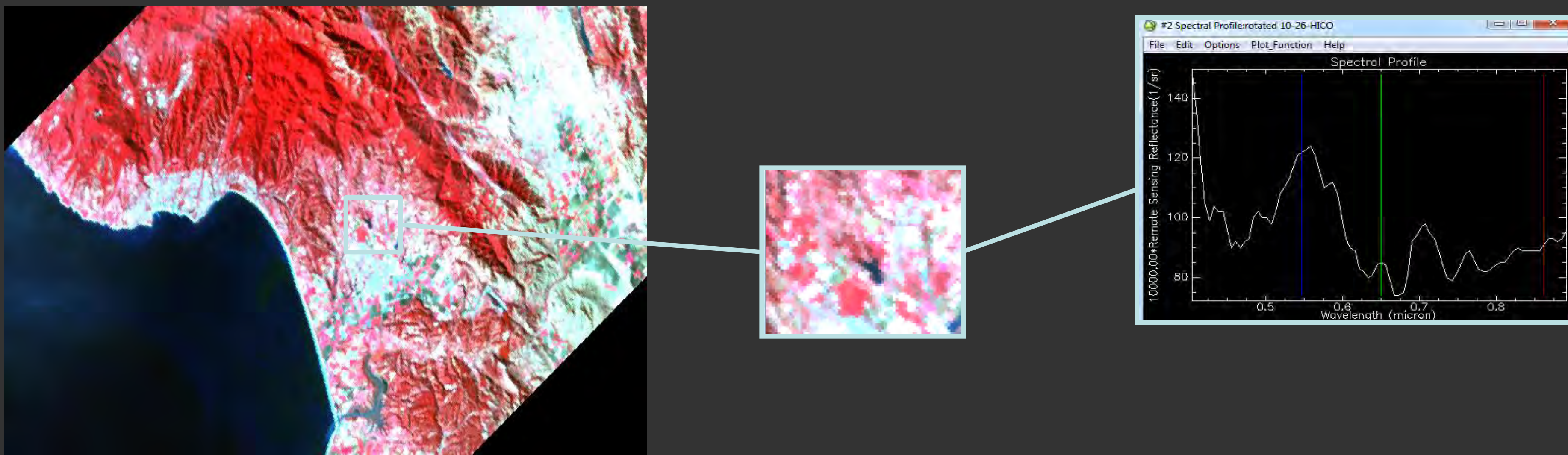
Creation of indices & use on library species

- Identification of key spectral features
- Feature x-value, y-value, height, width, area
- Ex. index, (peak 1 height/peak 2 height) = $\frac{(R565 - R625)}{(R655 - R625)}$





Indices applied to HICO match field data



- Indices applied 10/26/2011 HICO data suggest high biomass mixed bloom, consistent with 10/23 and 10/29 field data

Summary

- If the goal is to detect toxins at greater than regulatory limits for drinking water or recreational contact, many commercial kits and methods exist
- If the goal is to identify spatial/temporal variability of toxins, SPATT is ideal
- Other methods focusing on the presence of phycocyanin are promising, and can provide rapid assessment of potential blooms