

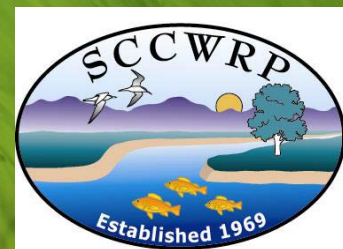
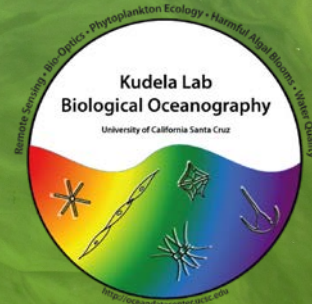
# Monitoring and Assessment Tool: Solid Phase Adsorption Toxin Tracking (SPATT)

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University of California, Santa Cruz

Meredith Howard

Southern California Coastal Water Research Project



# Recurrent Known Blooms and Cyanotoxin Hotspots in California Prior to 2011

**Klamath River**



**Clear Lake**

**San Francisco Bay area /Delta**

**Monterey Bay/Pinto Lake**



# Record Breaking Years 2014 - 2016

- Record high microcystin concentrations detected
- Record number of lakes closed for recreation
- Several dog deaths attributed to cyanotoxins
- Multiple toxins detected simultaneously
- Fish kills caused by *Pyrmnesium parvum*

Bloom Last Verified  
11/1/2015 12/8/2016

## Northern CA:

Klamath Basin: >10 years

Trinity River: Anatoxin and Microcystins

Russian and Eel Rivers: dog deaths

## Central CA:

Lake Chabot: dog deaths

Clear Lake: 16,000  $\mu\text{g/L}$

East Bay Regional Parks: multiple lake closures

SFB and Delta: multiple toxins ~year-round

Pinto Lake: 2<sup>nd</sup> most toxic lake in the world; ongoing blooms; 1<sup>st</sup> closure

## Southern CA:

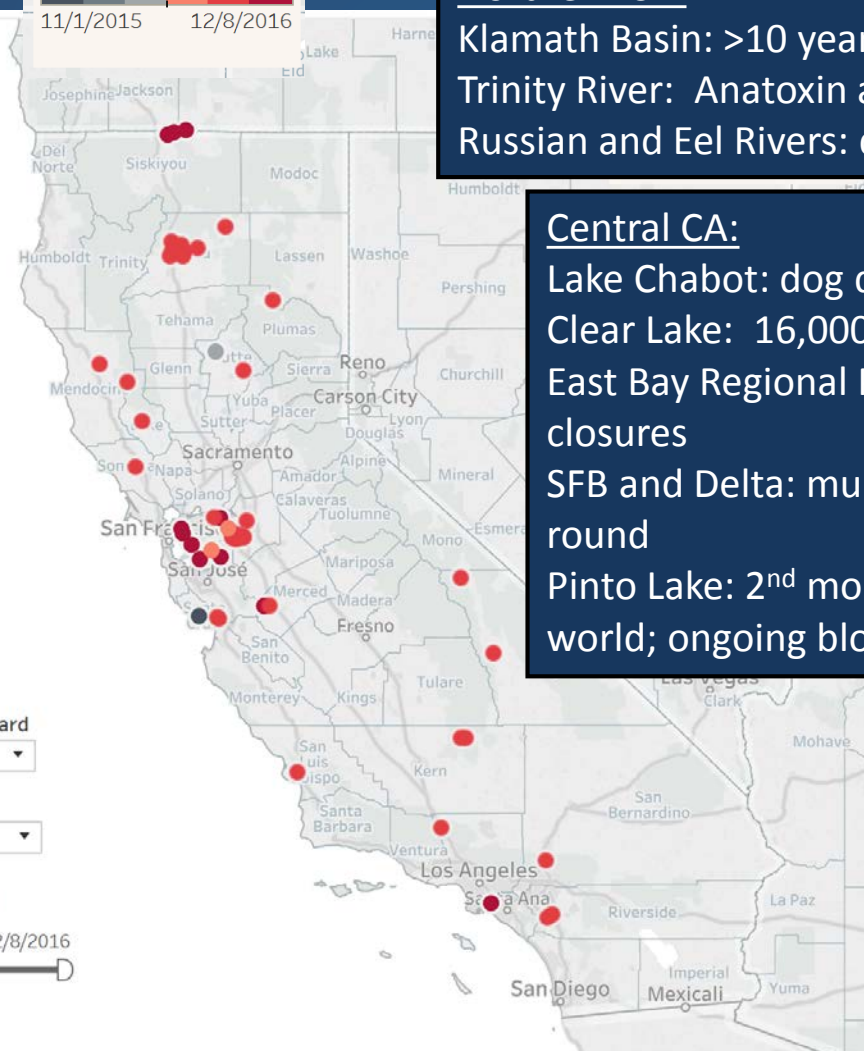
Lake Elsinore: Multiple toxins > health thresholds

San Joaquin Marsh, 33,500  $\mu\text{g/L}$

Canyon Lake: multiple toxins >health thresholds

Suspected deer and mountain lion deaths

Fish kills from *P. parvum* at multiple lakes



# A Tour of California Hotspots



Lake Elsinore—5,000  $\mu\text{g/L}$   
Scum: MCY 95,000  $\mu\text{g/L}$ ; CYL 181  $\mu\text{g/L}$ ; ANA 18.5  $\mu\text{g/L}$



Lake Chabot—11,000  $\mu\text{g/L}$ ;  
800,000  $\mu\text{g/L}$  scum



Pinto Lake—1,000  $\mu\text{g/L}$  annually;  
2.9 million  $\mu\text{g/L}$  scum



San Joaquin Marsh—33,500  $\mu\text{g/L}$

# A Tour of California Hotspots



## **Wadeable Streams:**

Microcystin—33%

Lyngbyatoxin—21%

Saxitoxin—7%

Anatoxin-a—3%

## **Eel River algal mats:**

Anatoxin-a—42%

Microcystins—15%

Both—5%

ATX ~ 10x > MCY

Data Sources: Fetscher et al. *Harmful Algae* 49: 105-116

Bouma-Gregson & Higgins, Eel River Recovery Project Report 2015

# WADING INTO DANGER

Growth of toxic algae could make California's lakes unsafe

Extent of public health effects 'unknown'

SAN GABRIEL VALLEY TRIBUNE

## ALGAL BLOOMS

News Sports Entertainment Lifestyle Obituaries Opinion The Canniforn

Home News Algal blooms

People got sick at Pyramid Lake before the state reported toxic algae bloom. Could it have been avoided?

Stephanie K. Baer (Southern California News Group)  
<http://projects.sgvtribune.com/blue-green-algae/>

NEWS

### LAKE ELSINORE: Harmful blue-green algae forces area closure

All recreation is suspended on what is Southern California's largest natural freshwater body.

G+1 Like Share Tweet

Email Share

By MICHAEL J. WILLIAMS / STAFF WRITER

Published: July 28, 2016 Updated: July 29, 2016 7:56 a.m.

SFGATE NEWS SPORTS BUSINESS A&E FOOD LIVING TRAVEL REAL ESTATE CAR

### After dog dies, Labor Day revelers may have to avoid Russian River

By Henry K. Lee Updated 9:05 am, Friday, September 4, 2015

Email Facebook Twitter Pinterest Reddit Google+

7

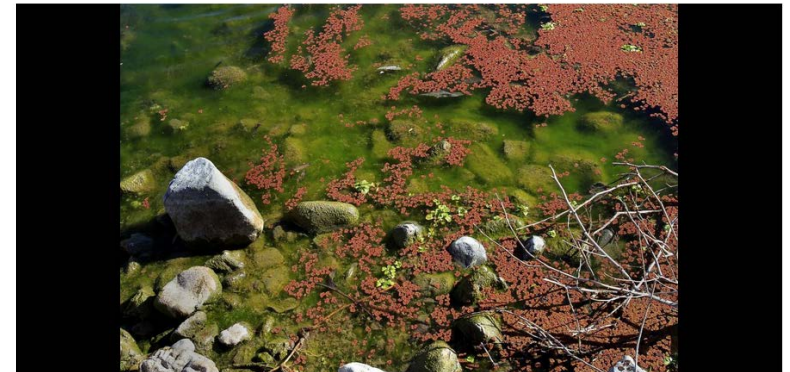


Photo: Brant Ward, The Chronicle

# 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.”

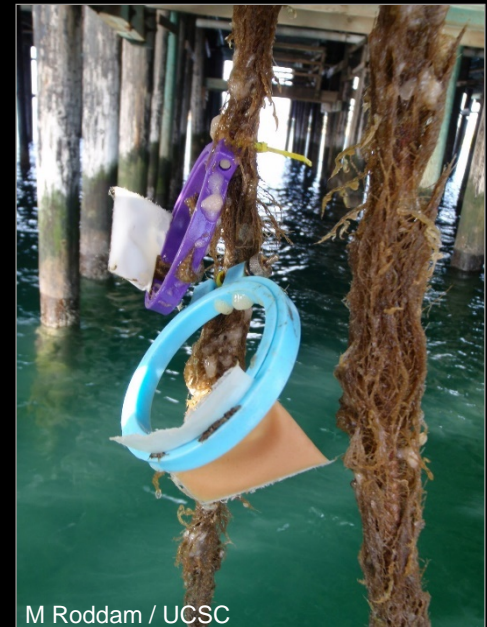
*MacKenzie et al. (2004) Toxicon*



K Borchers / San Jose Mercury News



M Roddam / UCSC



M Roddam / UCSC

# Solid Phase Adsorption Toxin Tracking (SPATT)

- Has been used in many areas of the world for the monitoring of dissolved algal toxins
  - Anatoxins (Wood et al 2011)
  - Azaspiracids (Fu et al 2009)
  - Dinophysistoxins (Fu et al 2008, 2009, Pizarro et al 2013)
  - Domoic acid (Lane et al 2010)
  - Microcystins (Kudela 2011)
  - Okadaic acid (MacKenzie et al 2004, Fu et al 2008, 2009)
  - Pectenotoxins (MacKenzie et al 2004, Fu et al 2009)
  - Saxitoxin (Lane et al 2010)
  - Spirolide toxins (Fu et al 2009)
  - Yessotoxins (MacKenzie et al 2004, Fu et al 2009)





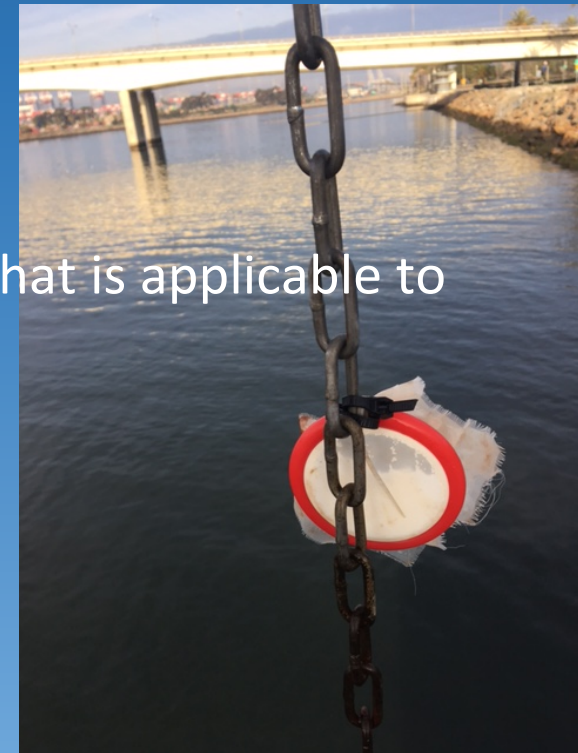
# Why Use SPATT?

## Advantages:

- Passive Sampler that is time-integrative
- Provides continuous toxin detection to capture ephemeral events that discrete samples can miss
  - Enhanced sensitivity at low ambient concentrations
- Applicable in all waterbody types and for many different toxins
- Low cost, simple and easy to deploy/recover

## Disadvantages:

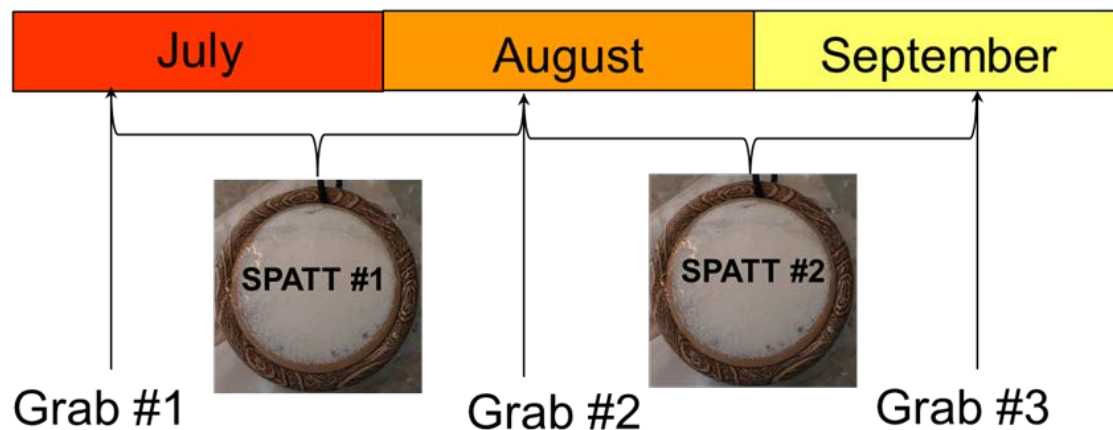
- SPATT will not provide a concentration of toxin that is applicable to health advisory thresholds (ng/g)
- Only measures dissolved toxins not total toxins



# Why Use SPATT?

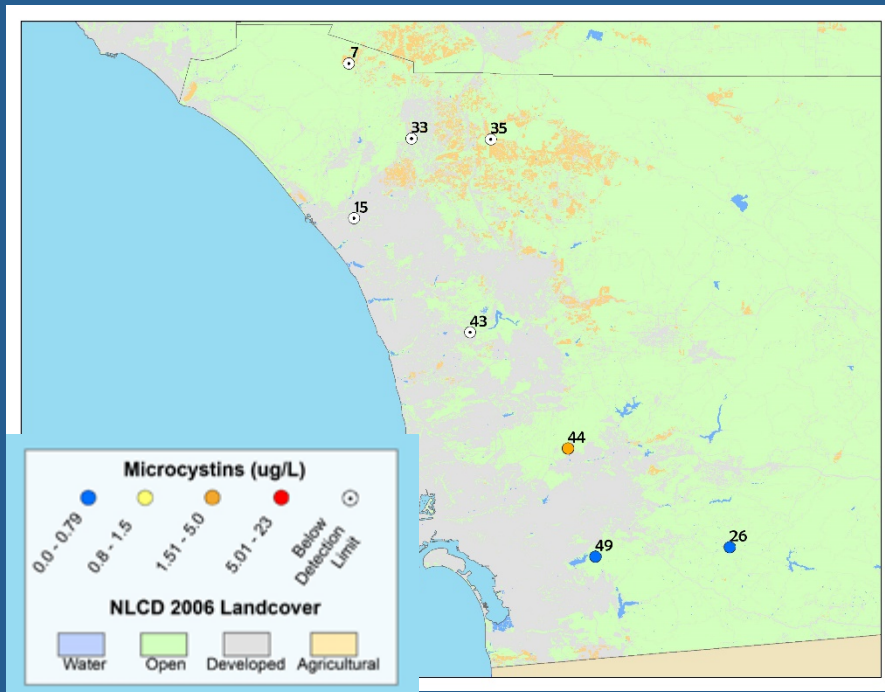
## Determine Toxin *Prevalence*

- Condition assessments and screening studies
- Waterbodies with little to no HAB data
- Determine the prevalence of toxin across a region
  - Depressional wetlands assessment (probabilistic design)
  - Lakes, estuaries and reservoirs (targeted design)

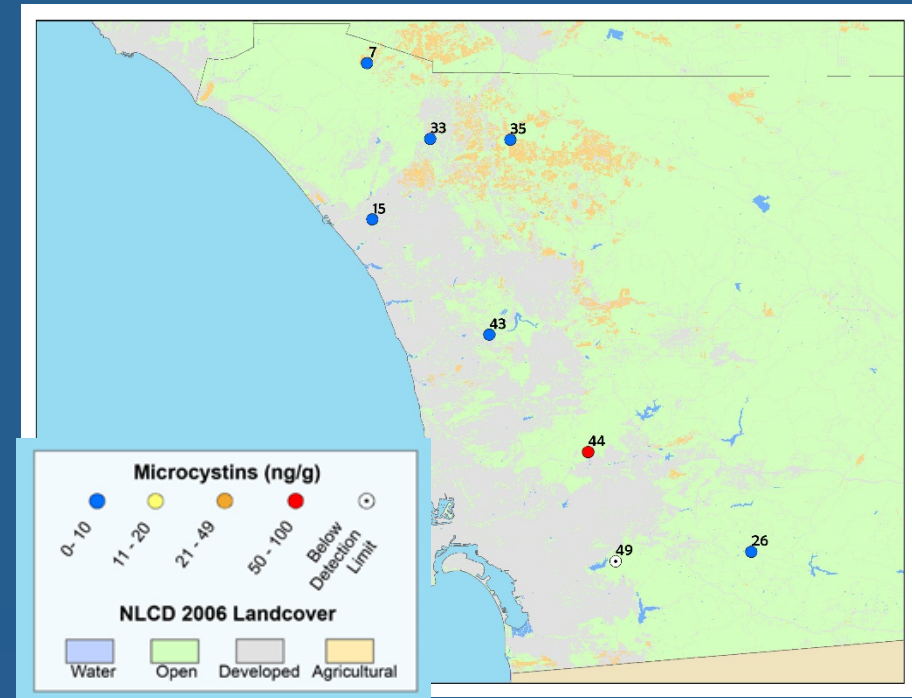


# Microcystin Prevalence Underestimated From Grab Samples By ~50%

Grab Samples



SPATT Samples



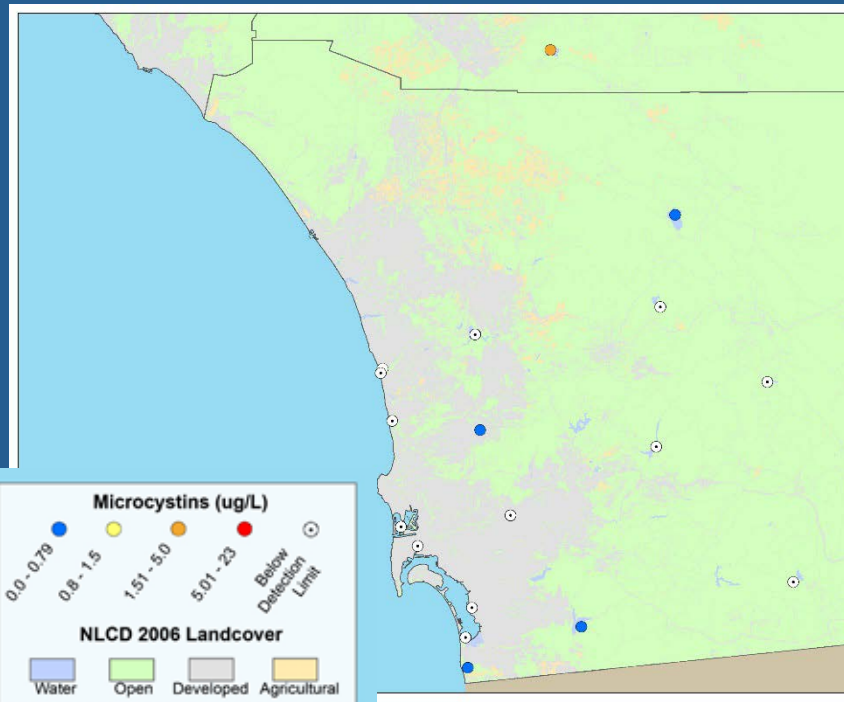
## % of Toxic Sites: Depressional Wetlands

Grab Samples	29%
SPATT Samples	83%

# Microcystins Detected at Every Site Sampled

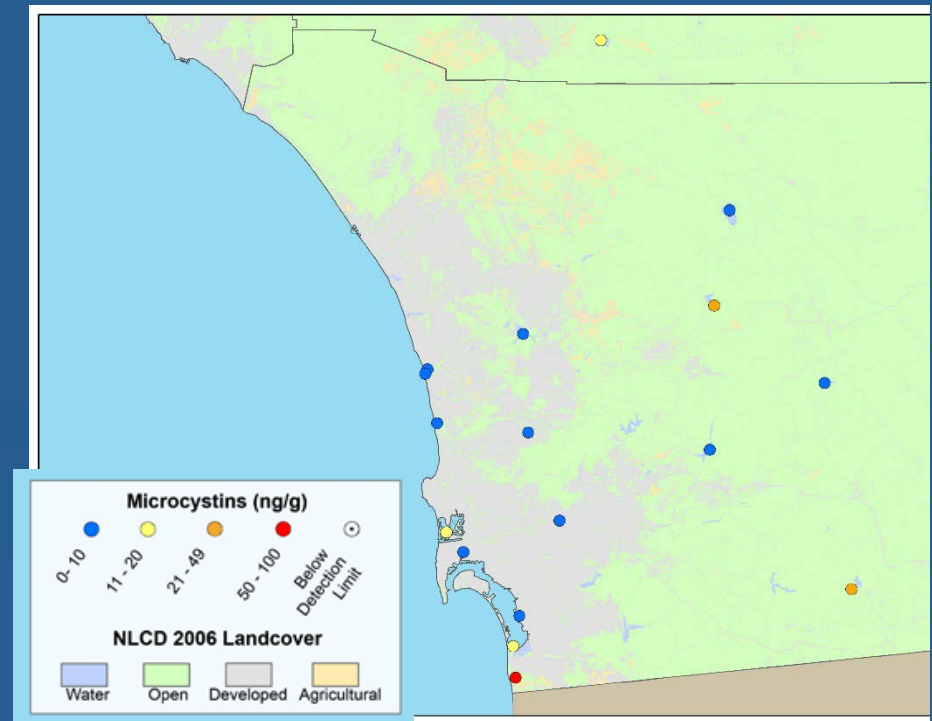
San Diego County: Lakes, Reservoirs, Estuaries and Coastal Lagoons

## Grab Sample Results



## SPATT Sample Results:

**All sites toxic**





# Why Use SPATT?

## Deploy In Areas with Limited Sampling

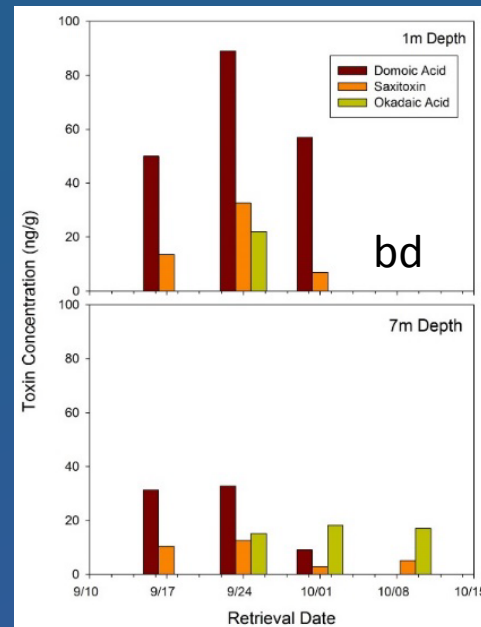
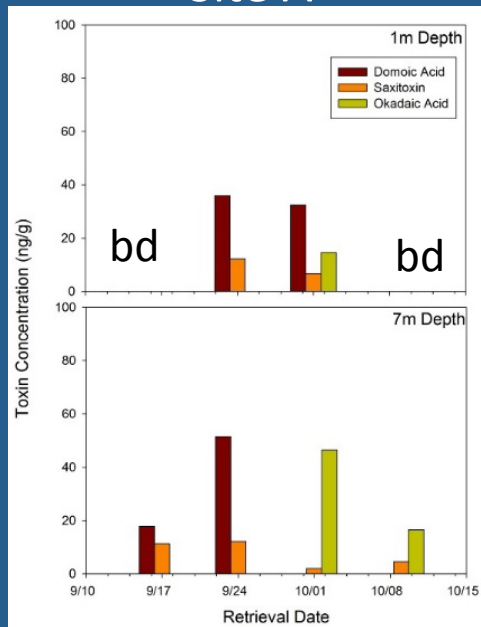


Site A

Site B

1 meter depth

7 meter depth

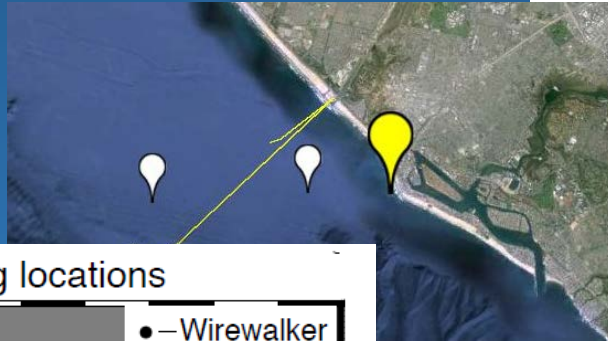


Pier:  
DA below detection

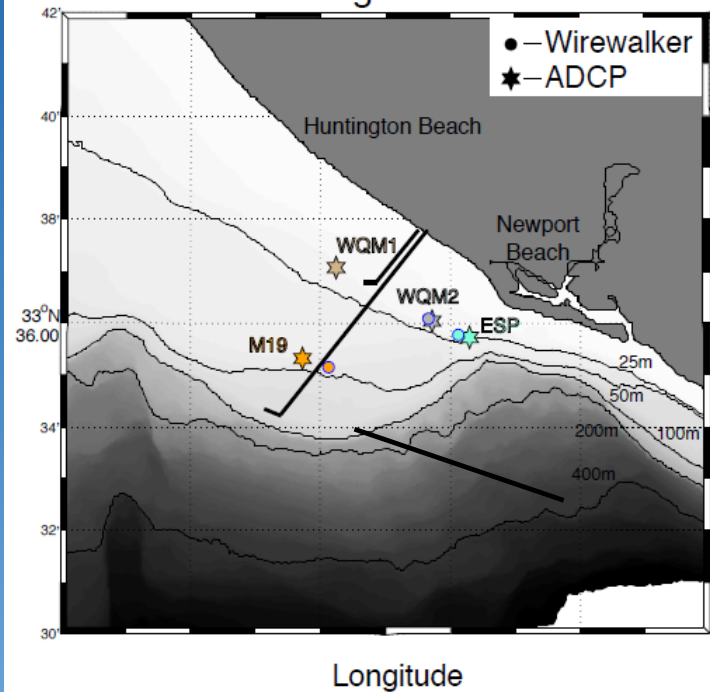
Domoic Acid  
 Saxitoxin  
 Okadaic Acid

Slide and data provided by Erica Seubert

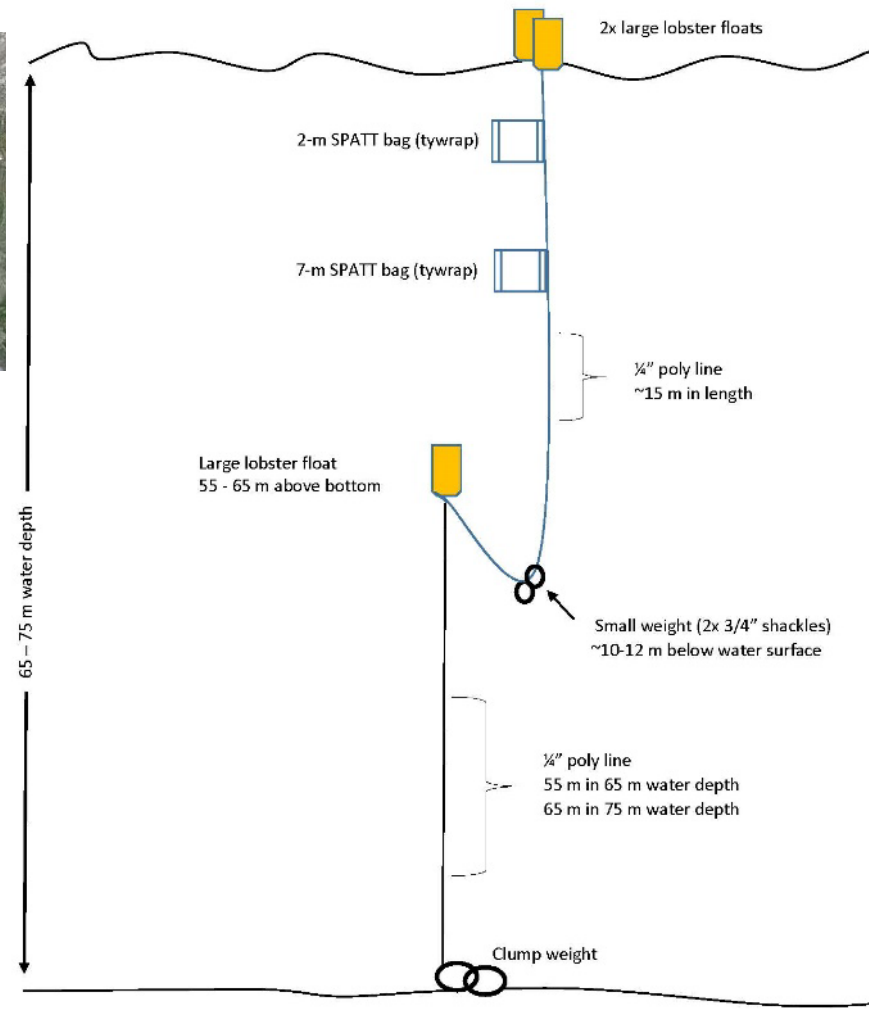
# SPATT Deployment: Buoy and Mooring



## Mooring locations

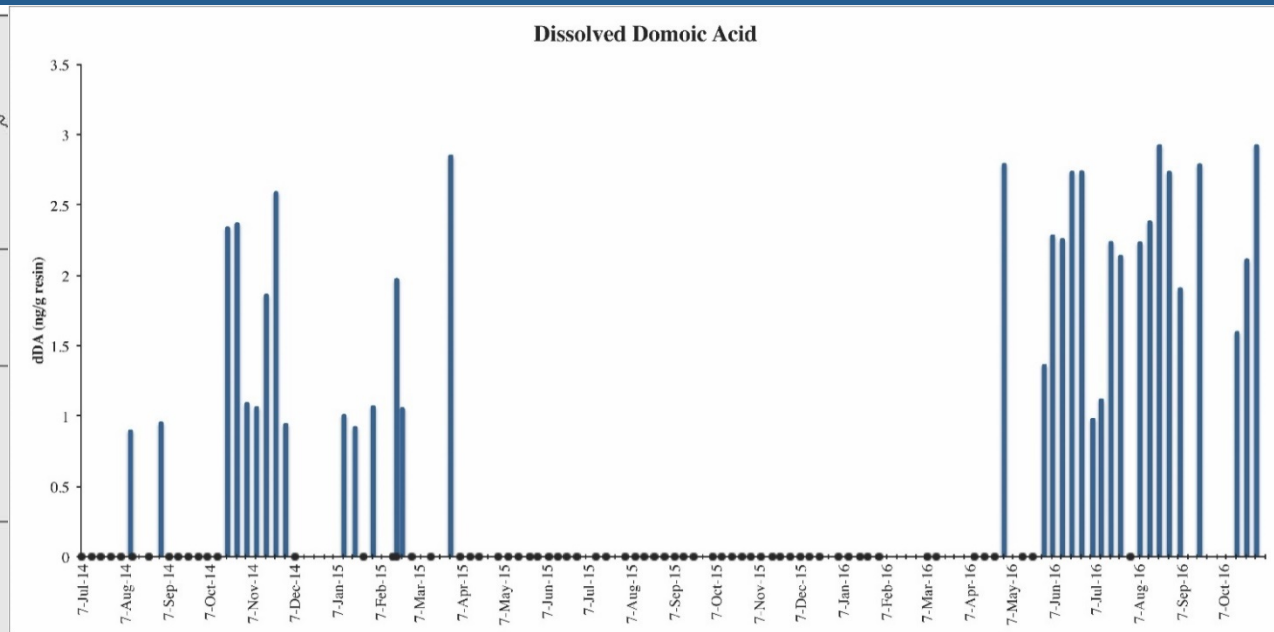
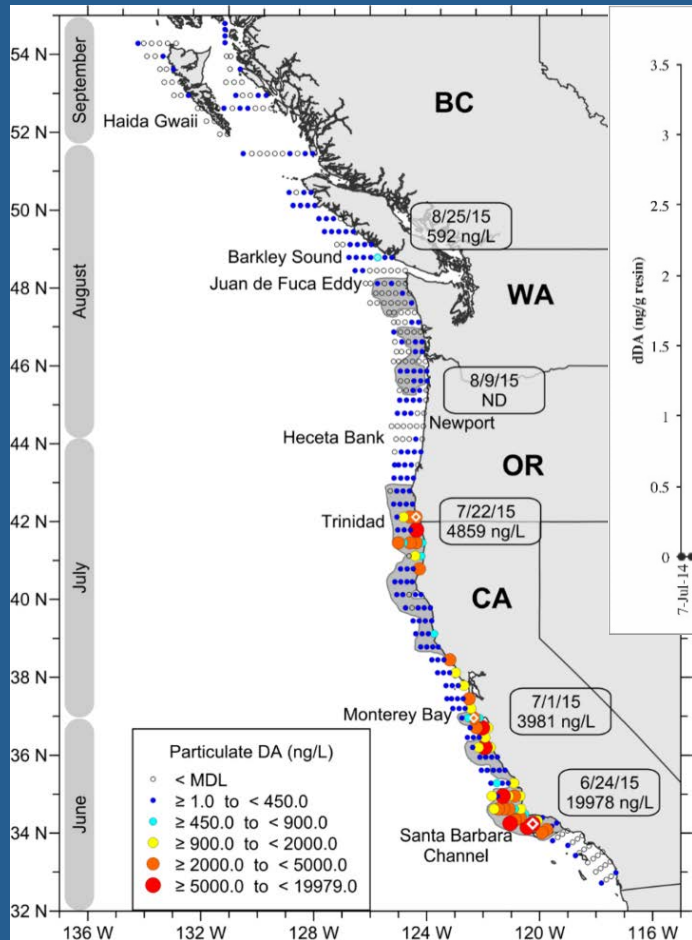


## Buoy Design



# Why Use SPATT?

## Continuous measurement of toxin



McCabe et al., 2016

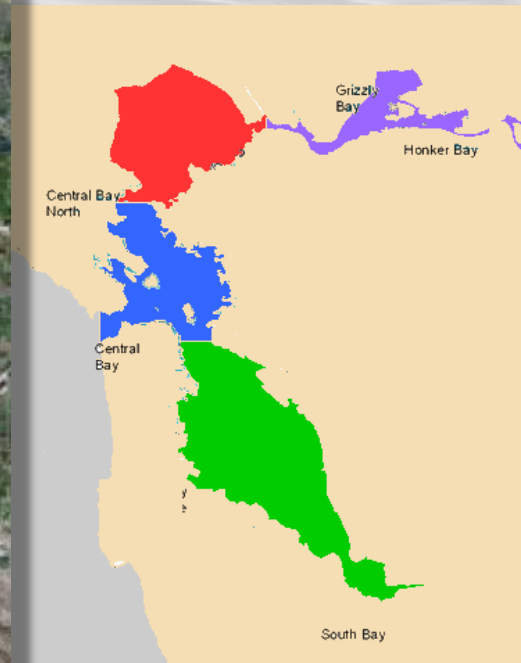
SPATT data provided by Jayme Smith and Dave Caron



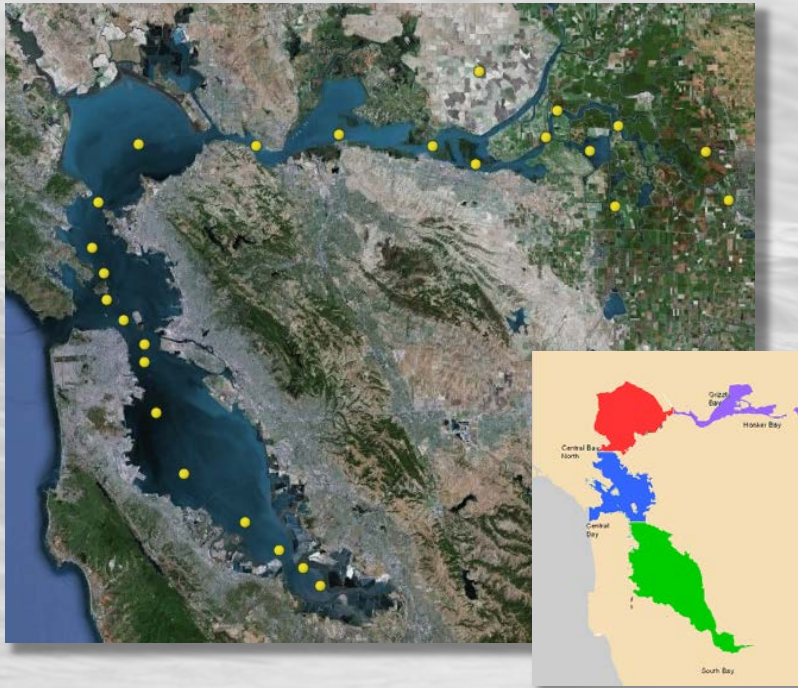
# Why Use SPATT?

## Uncovering Ubiquitous and Year Round Toxins

2011-2016: USGS Deployment of SPATT



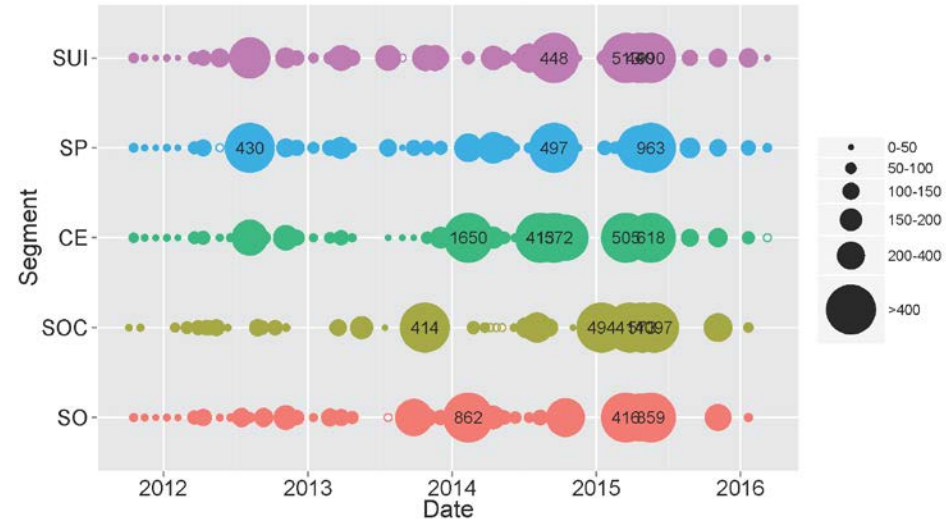
# San Francisco Bay



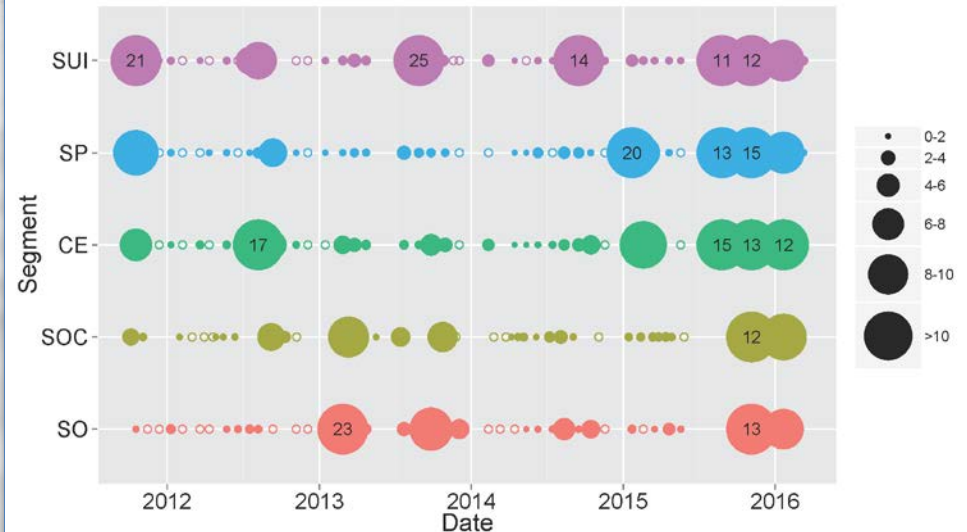
Focusing on SF Bay, we know that several algal toxins are nearly ubiquitous in the Bay.

The Bay seems to act as a mixing bowl for both freshwater and marine toxins...

## Domoic Acid From SPATT



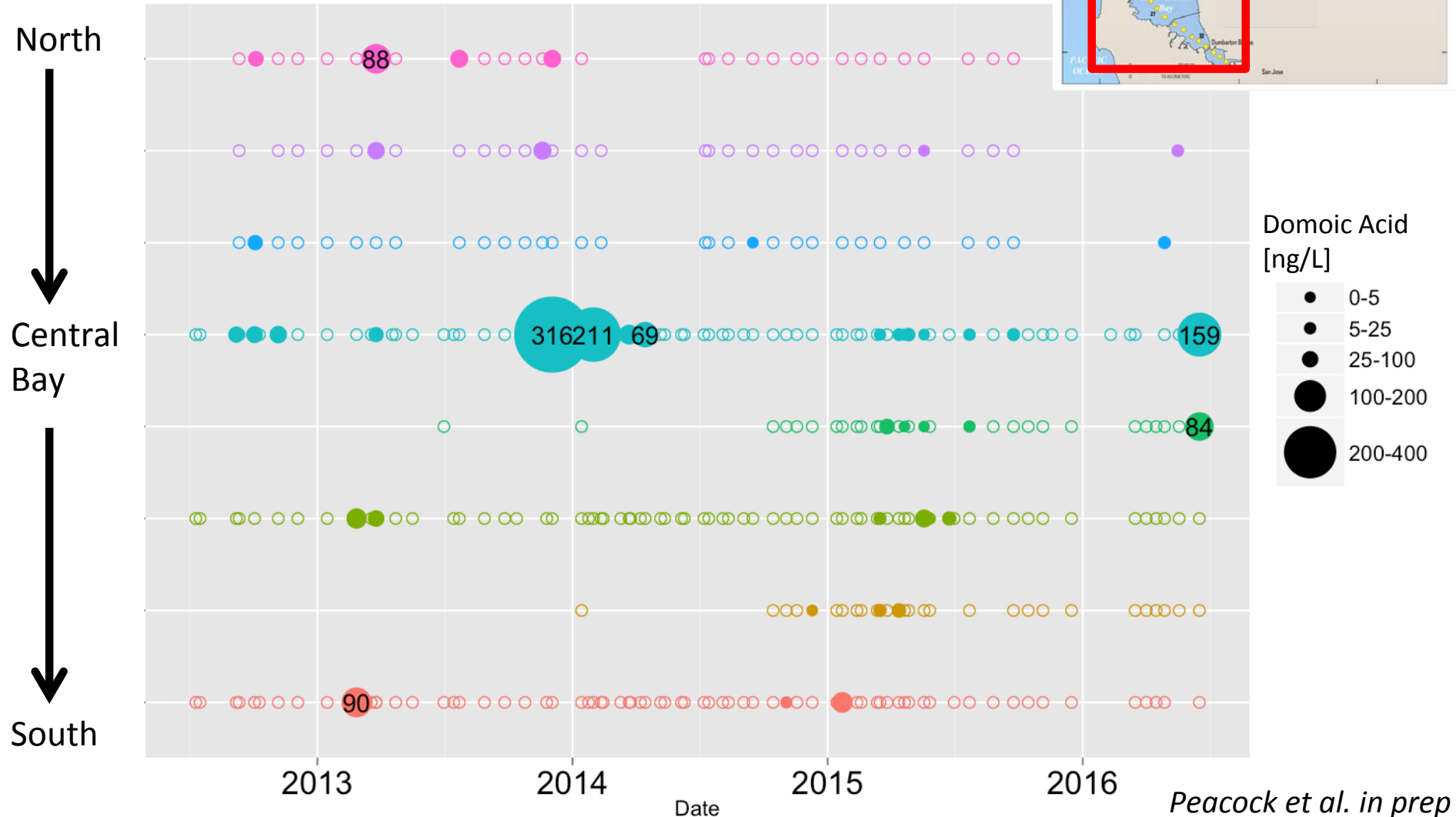
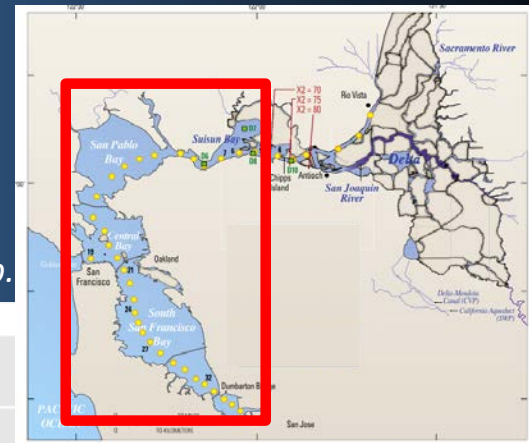
## Microcystins (LR-RR-YR-LA) From SPATT



# Particulate Domoic Acid



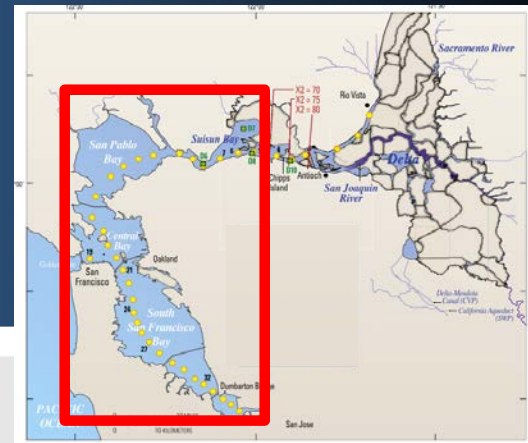
*Pseudo-nitzschia* spp.



# Dissolved Domoic Acid From SPATT



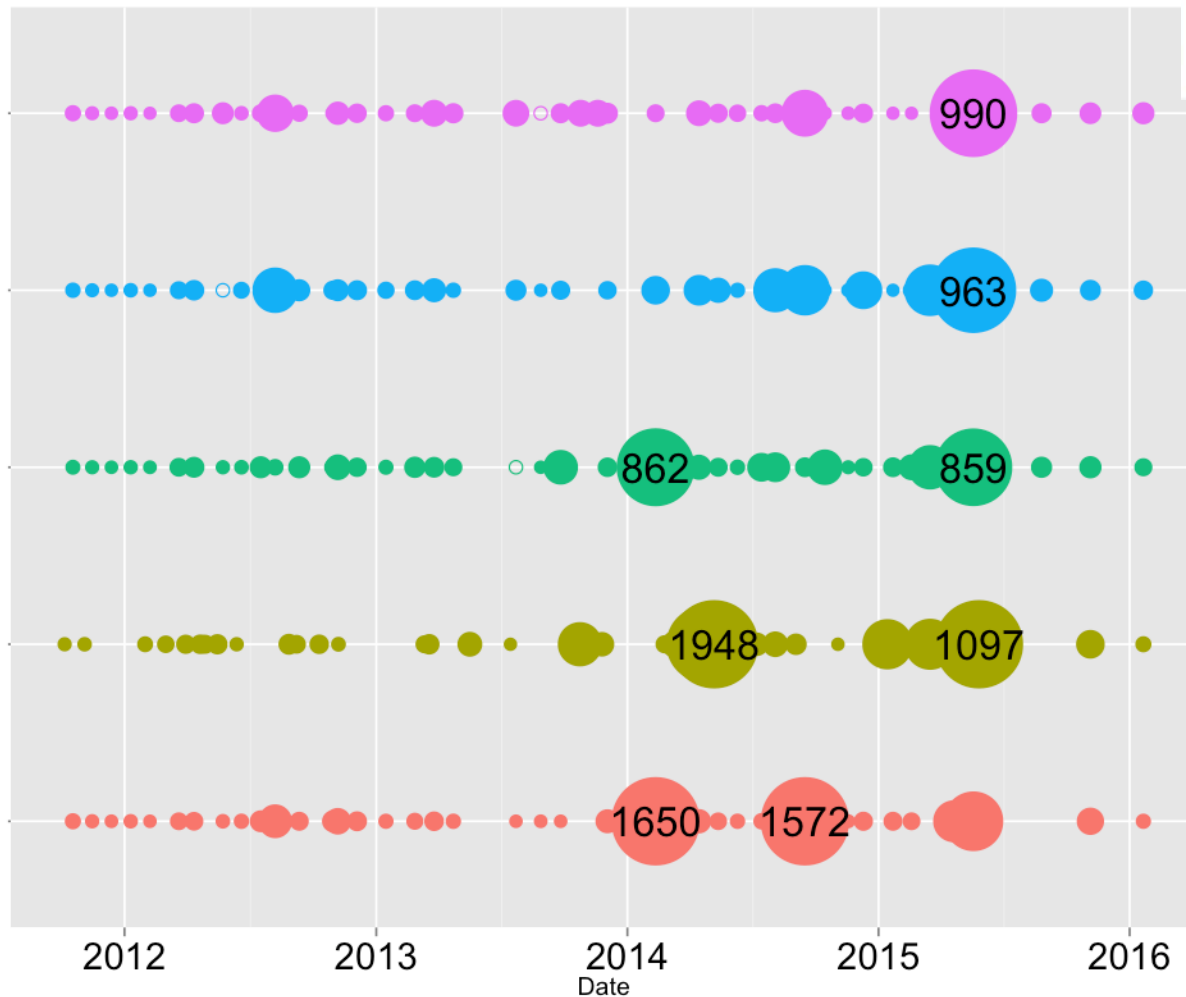
*Pseudo-nitzschia* spp.



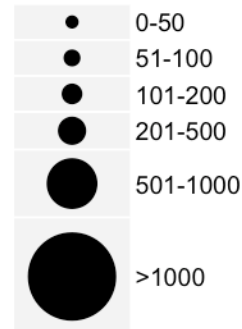
North

Central Bay

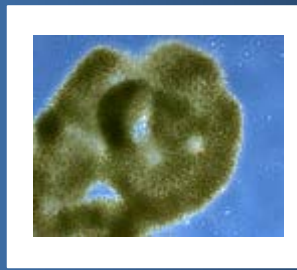
South



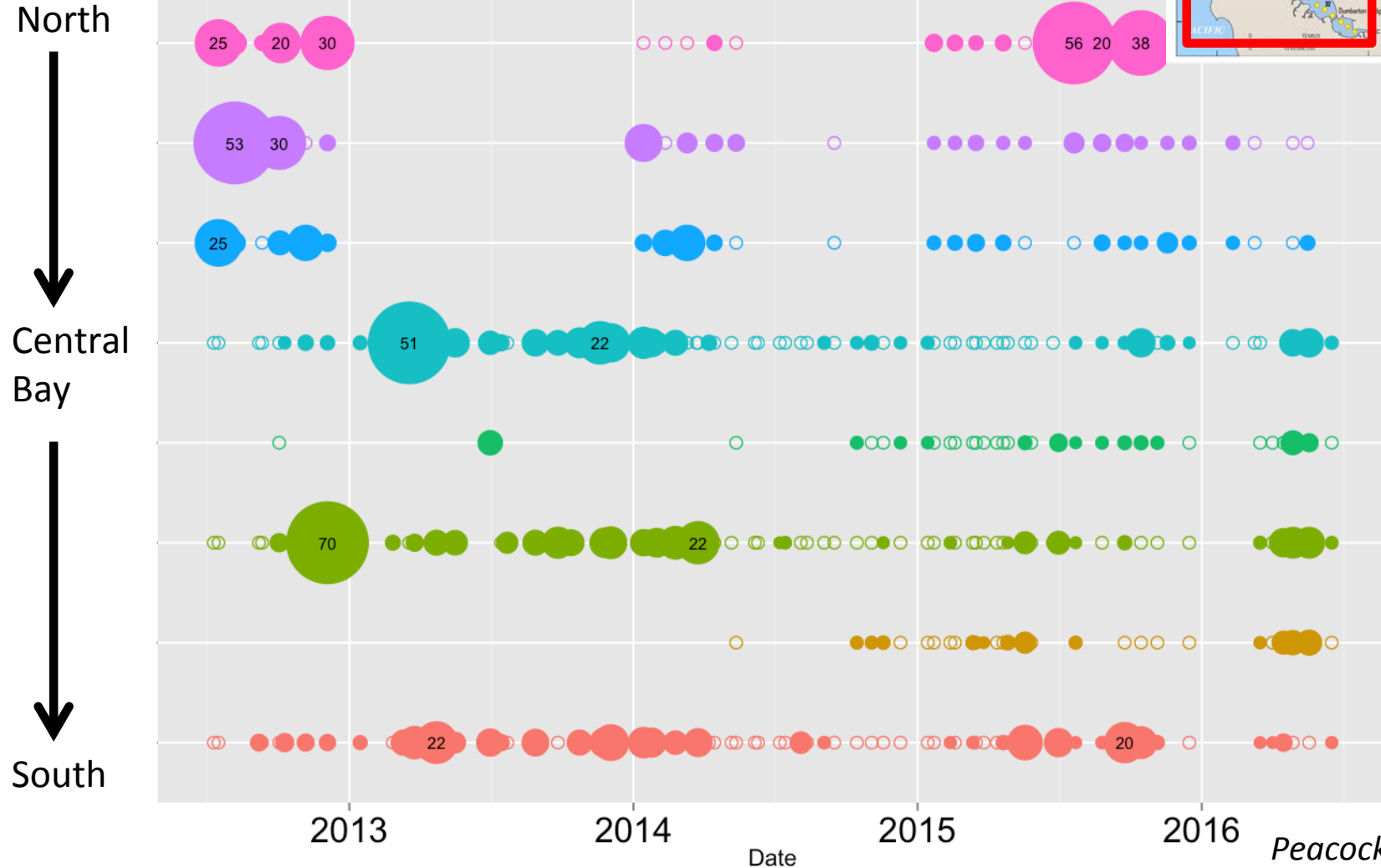
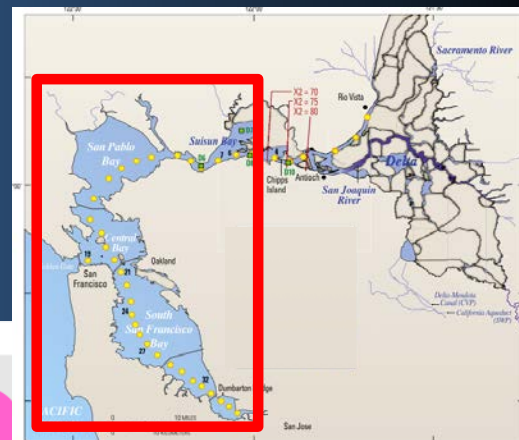
Domoic Acid [ng/g]



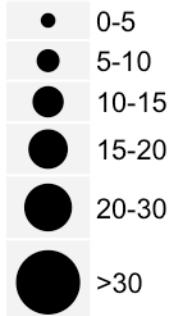
# Particulate Microcystin



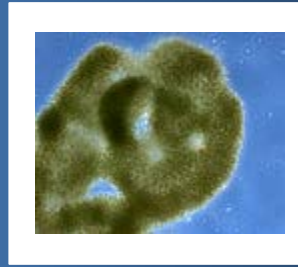
*Microcystis* spp.



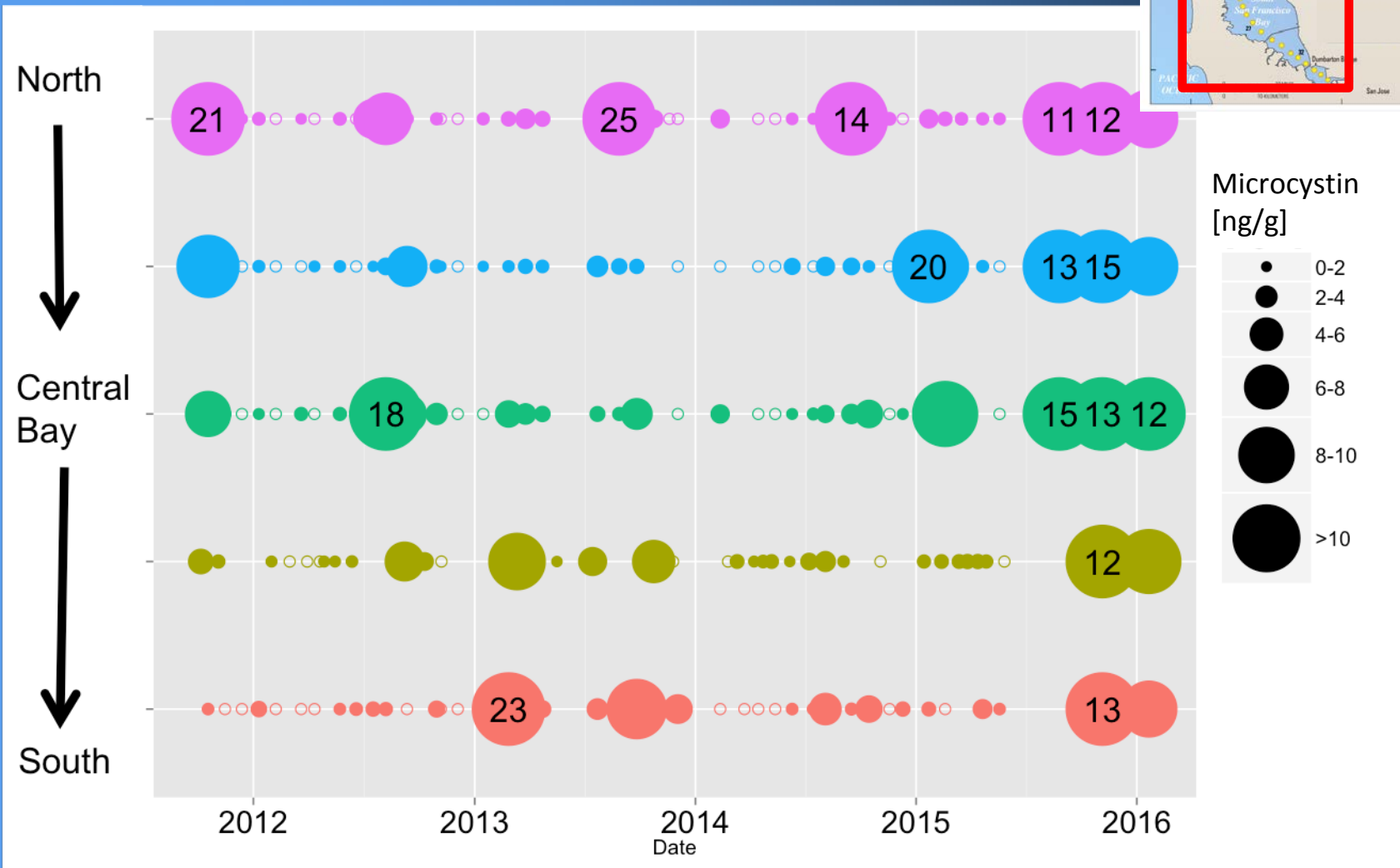
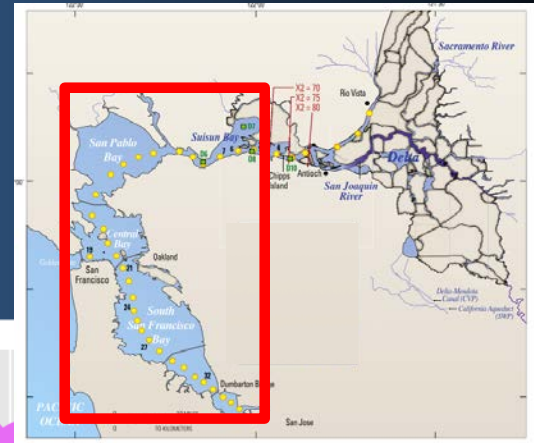
Microcystin [ng/L]



# Dissolved Microcystin From SPATT



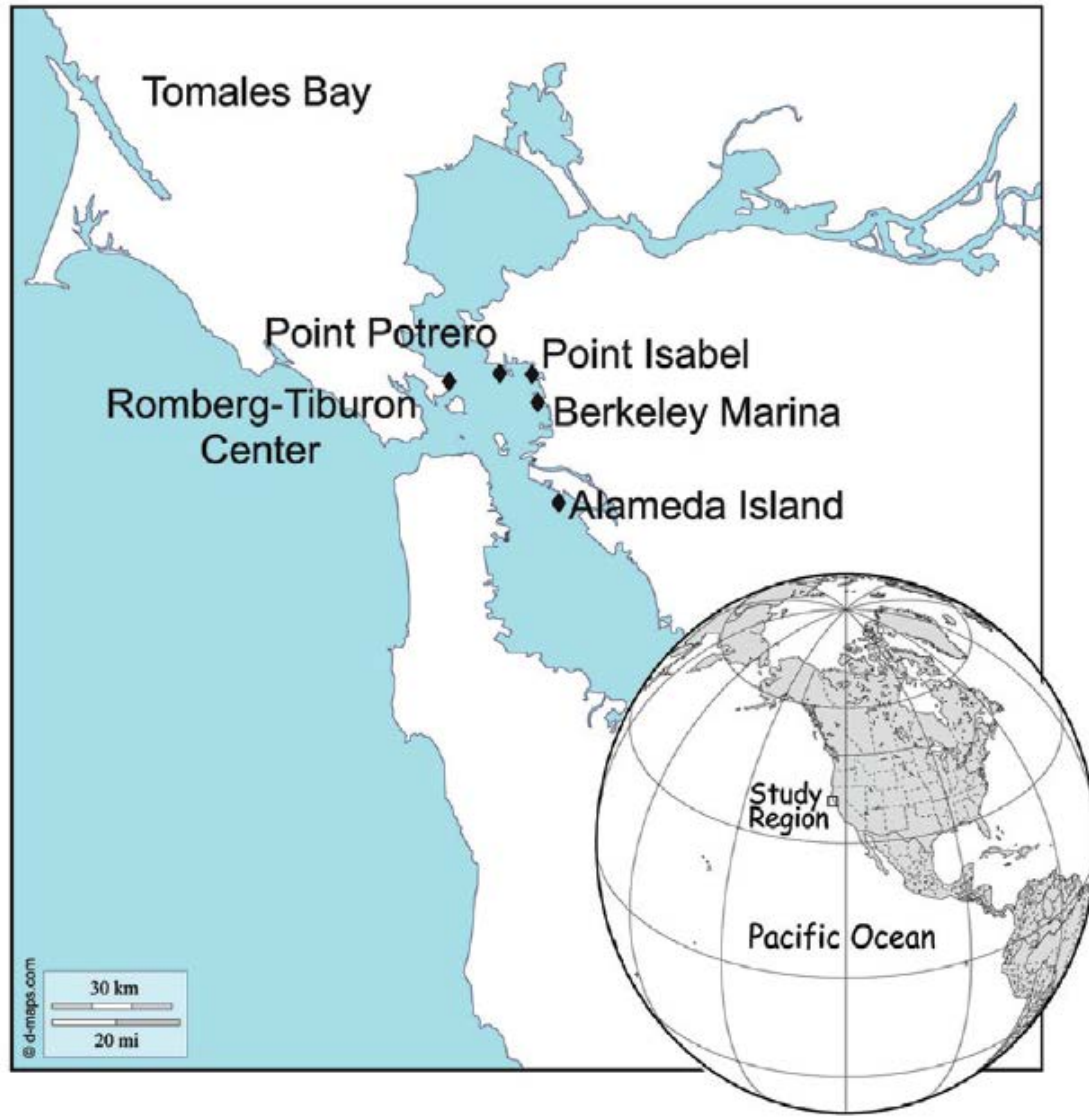
*Microcystis spp.*



# Deploy SPATT Using Ship Flow-Through System



# Mussel Collection



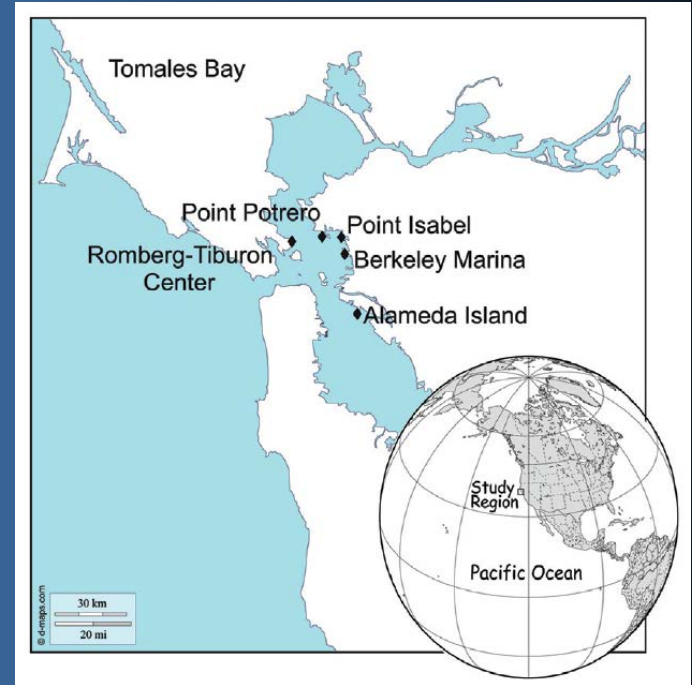
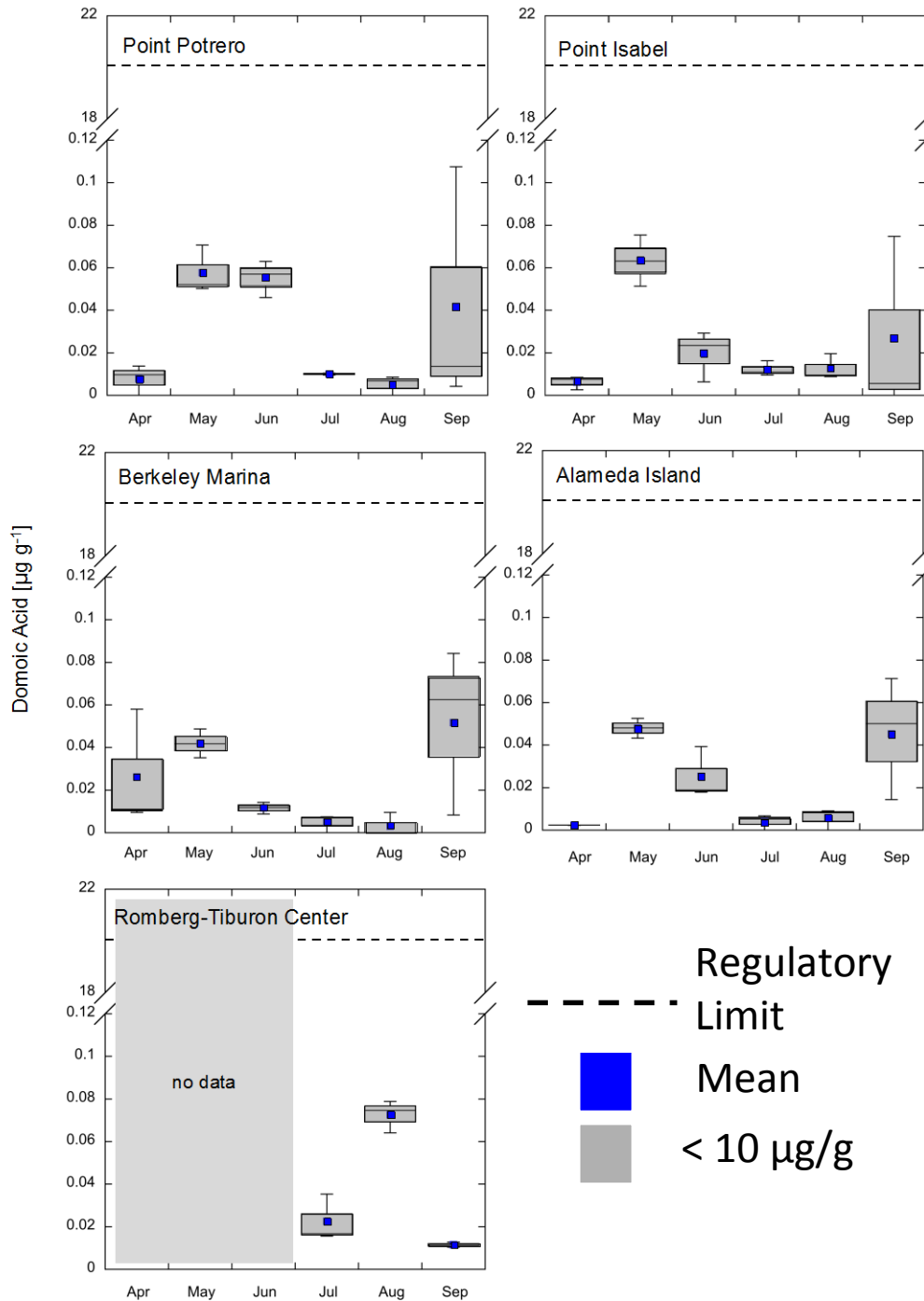
- Environmental mussel samples
- 5 locations, 1x per month
- April – September 2015
- Each mussel tested for Domoic Acid, Microcystin, PST, Okadaic Acid and DTX-2



California Mussel



# Domoic Acid in Mussels

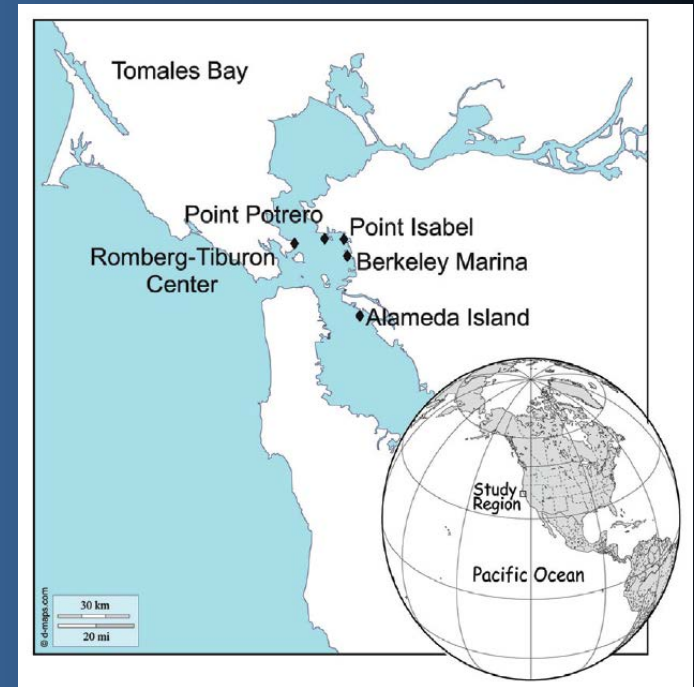
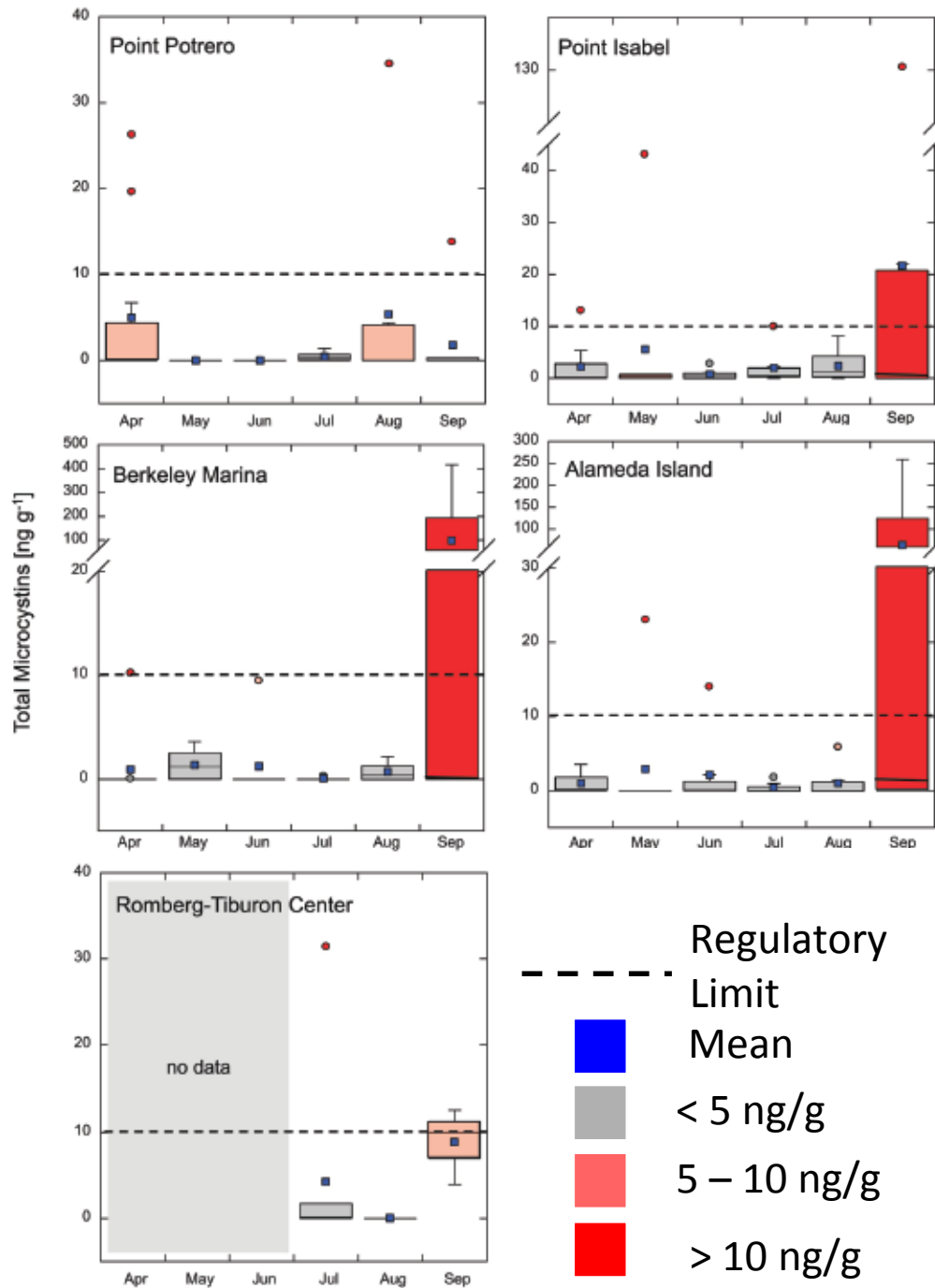


- Low but measurable DA
- Followed the trend of West Coast bloom
- But **NOT** the magnitude



Peacock et al. in prep

# Microcystins in Mussels



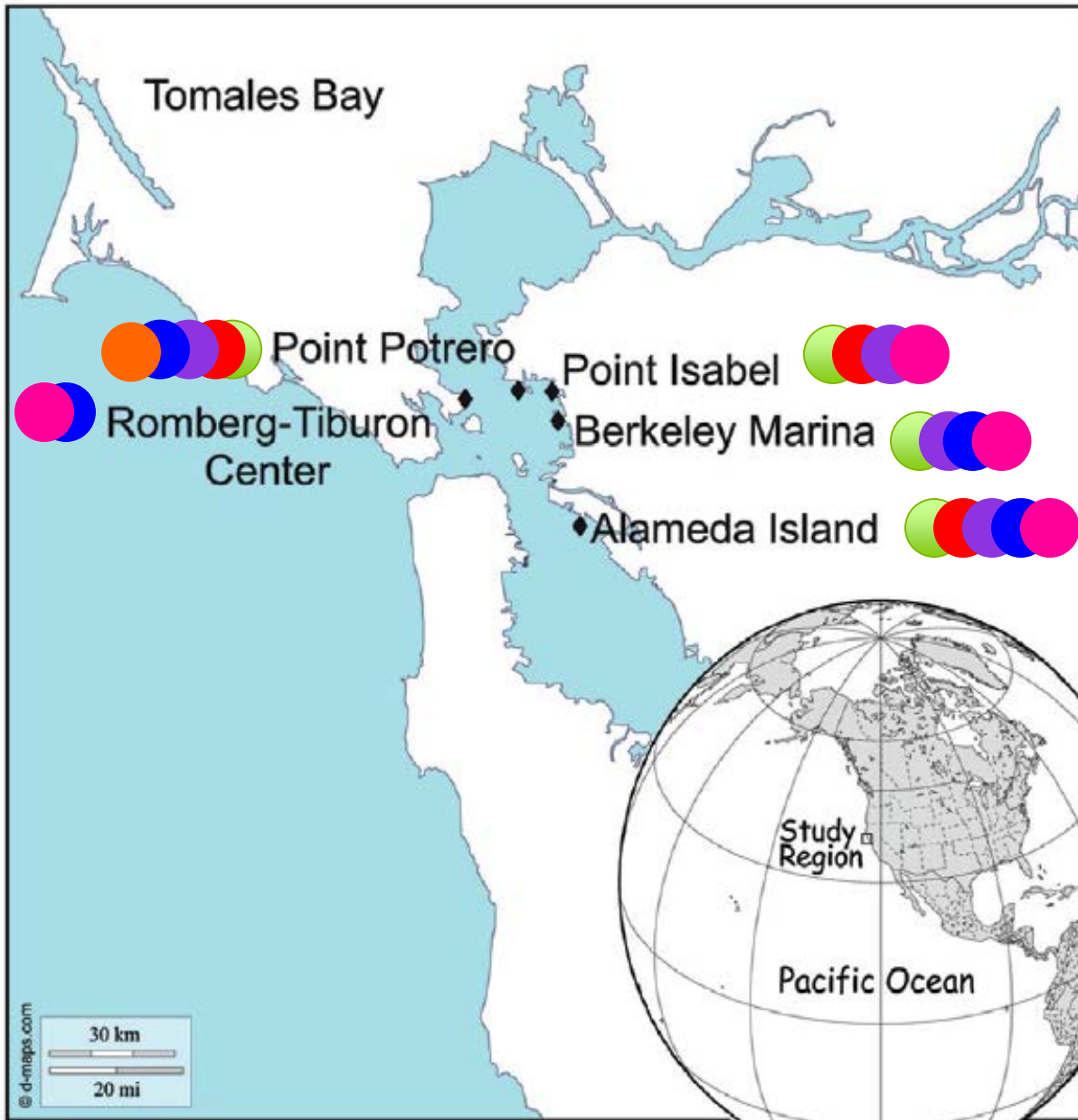
- Sometimes **HIGH** microcystin
- Variability
- No regulatory limit
- Are **NOT** monitored for



Gibble et al., 2016

# PST in Mussels

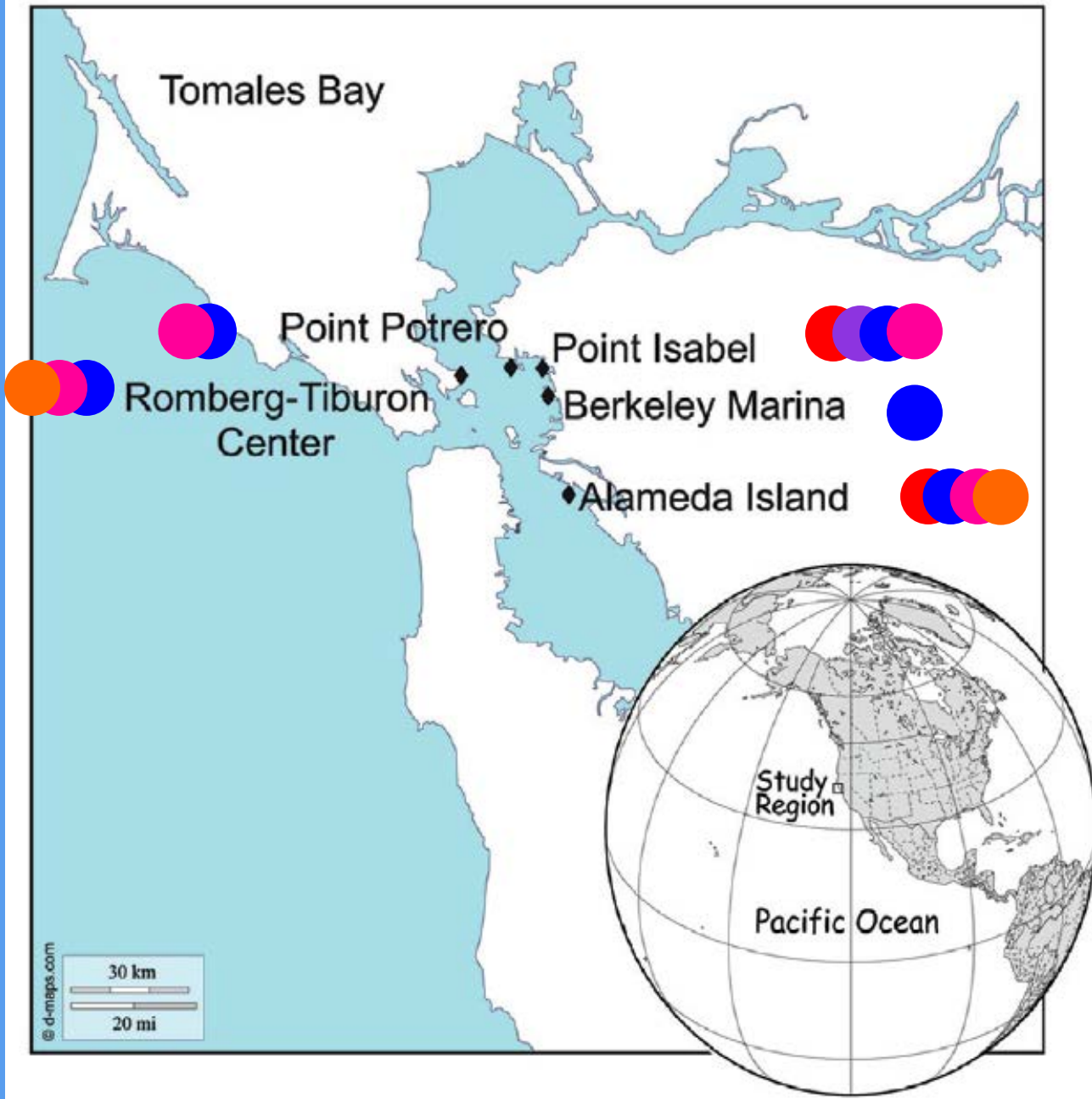
- Can be marine or freshwater toxins
- Low but measurable



- April
- May
- June
- July
- August
- September

# Okadaic Acid and DTX-2 in Mussels

- Sometimes **HIGH** OA and DTX
- Variability



- April
- May
- June
- July
- August
- September

# These toxins accumulate in the food web

## 2012, 2014 RMP Caged Mussels



Domoic Acid  
(**100%** of mussels contaminated)



Microcystins  
(**82%** of mussels contaminated)



Paralytic Shellfish Toxins  
(**59%** of mussels contaminated)



Okadaic Acid and DTX-2  
(**71%** of mussels contaminated)

# These toxins accumulate in the food web

## ~~2012, 2014 RMP Caged Mussels~~

Naturally occurring mussels, 2014-2016



Domoic Acid

(**100%** of mussels contaminated)  
100%



Microcystins

(**82%** of mussels contaminated)  
82%



Paralytic Shellfish Toxins

(**25%** of mussels contaminated)  
59%



Okadaic Acid and DTX-2

(**100%** of mussels contaminated)  
71%

# Why Use SPATT?

## *Persistence* of cyanotoxins flowing into marine waters

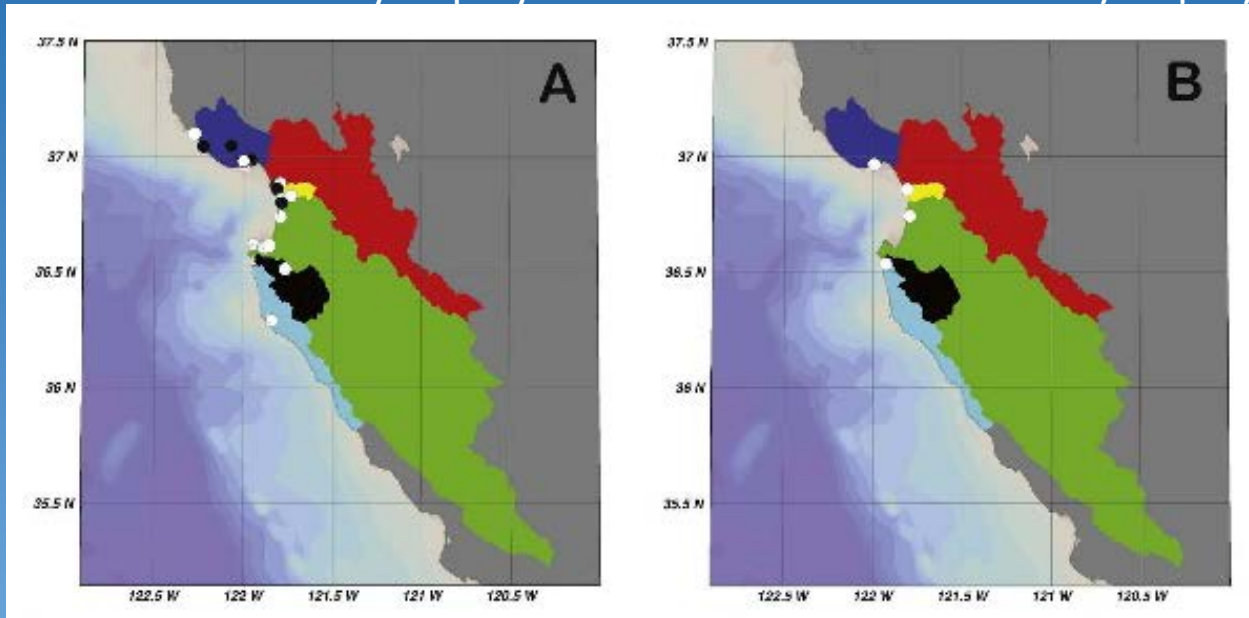
Do microcystins persistently flow into Monterey Bay from surrounding watersheds?

Answer: YES! Microcystins were persistently present over several years.

- Toxin peaks were in the spring and autumn seasons

2010-2011 Monthly deployments

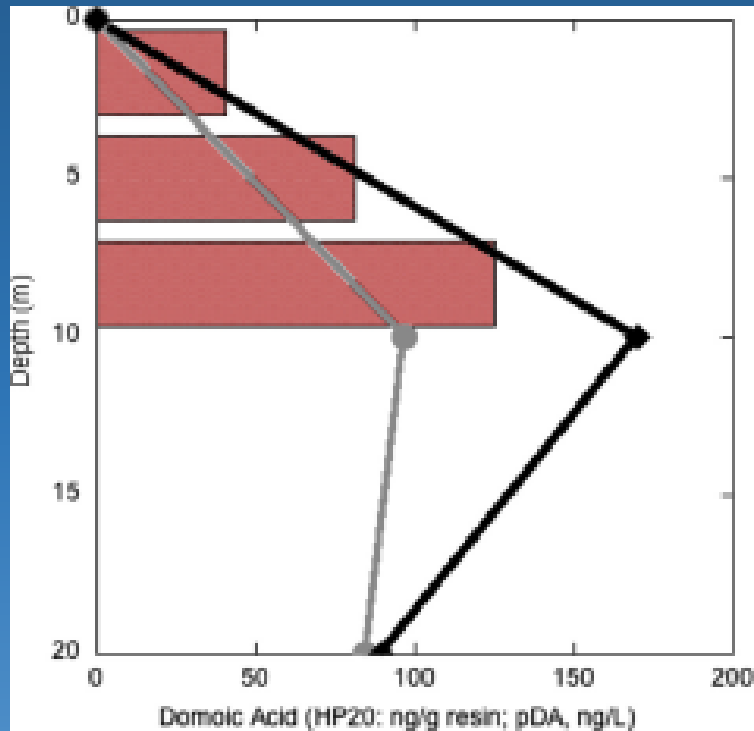
2011-2013 Weekly deployments



- Microcystins detected
- Microcystins not detected

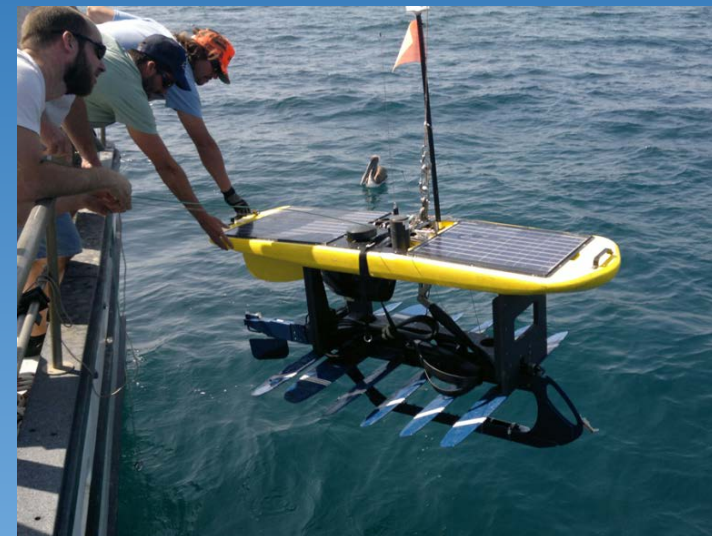
# SPATT Deployment: AUVs

## Liquid Robotics G5 surface wave glider



Berdalet et al., 2014

SPATT and Grab samples showed similar results: a persistent increase in DA



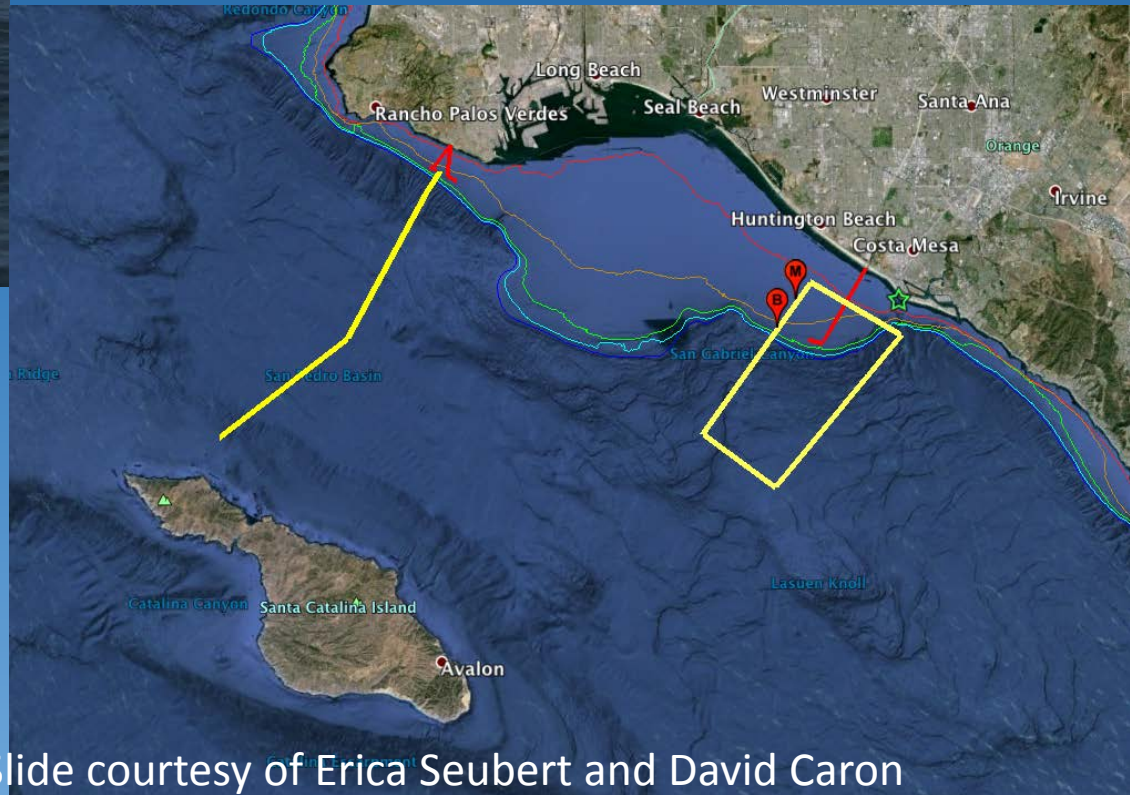


# SPATT Deployment: AUVs

## Teledyne Webb Slocum Gliders



SPATT detected domoic acid, saxitoxin;  
no okadaic acid detected



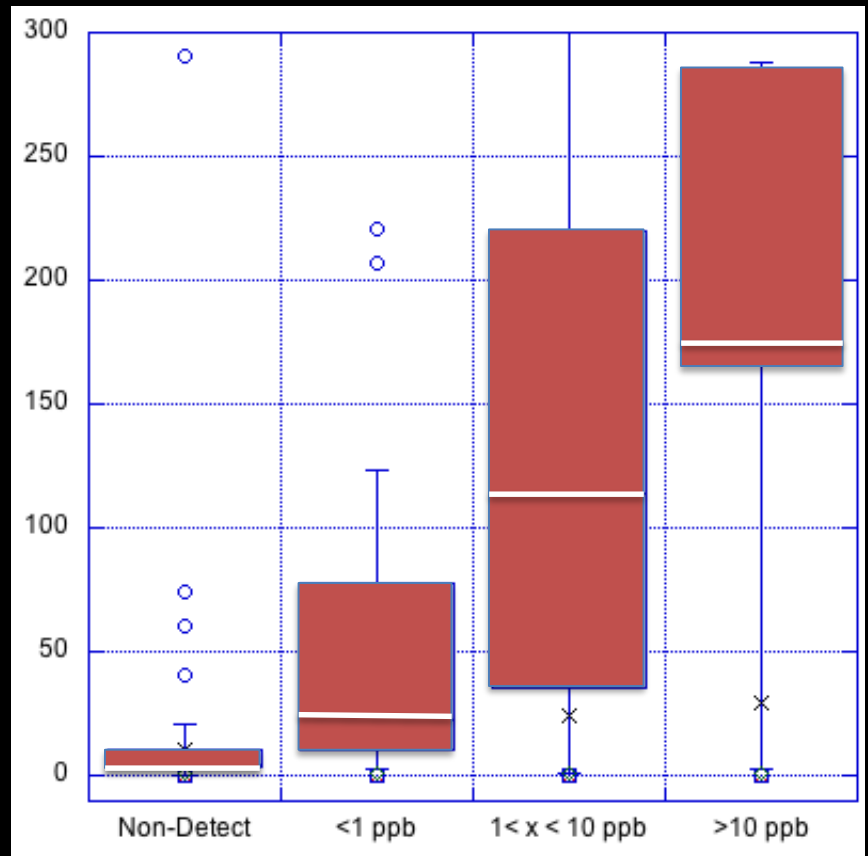
# Comparison of SPATT to Grab and Mussel Samples

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

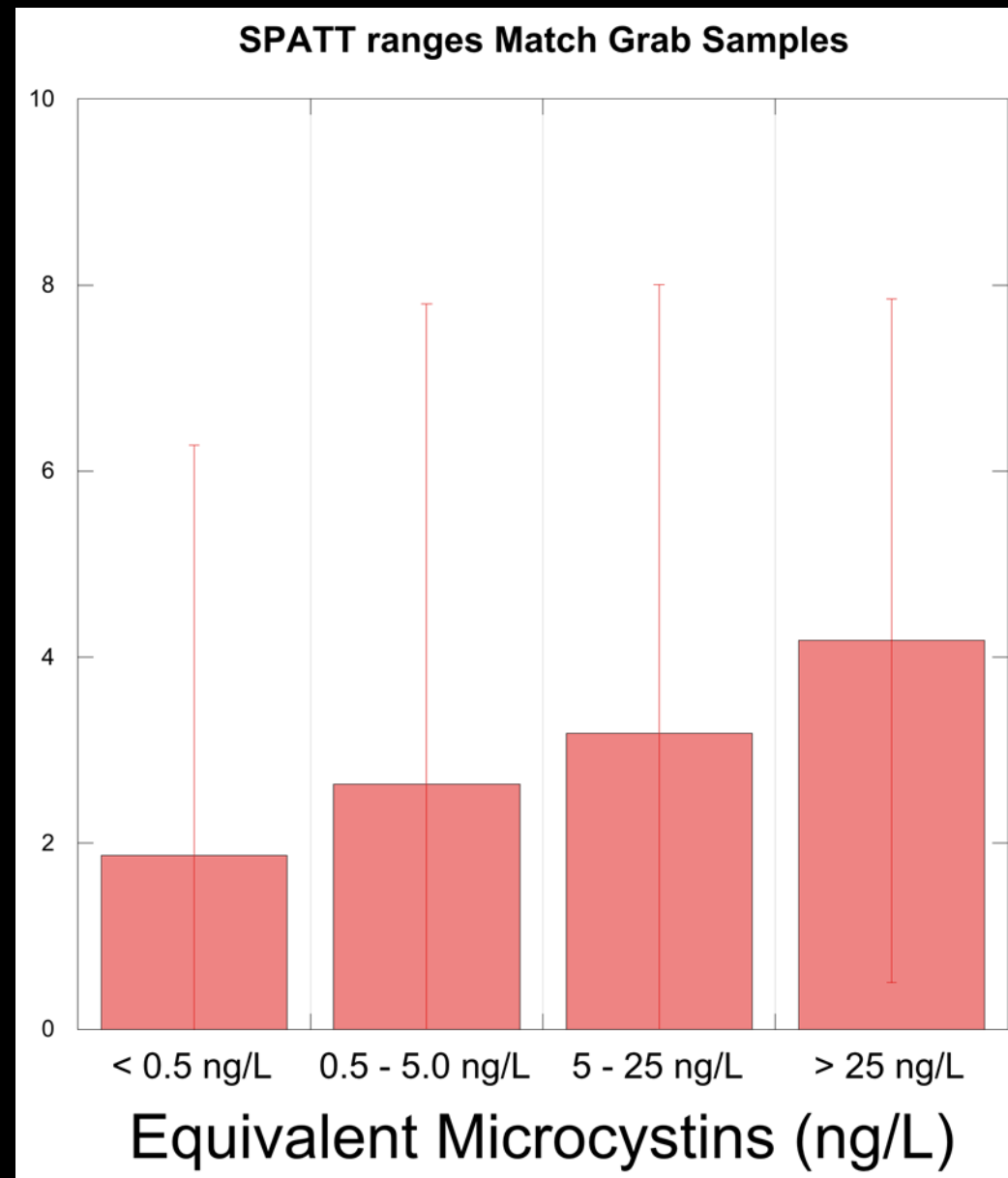
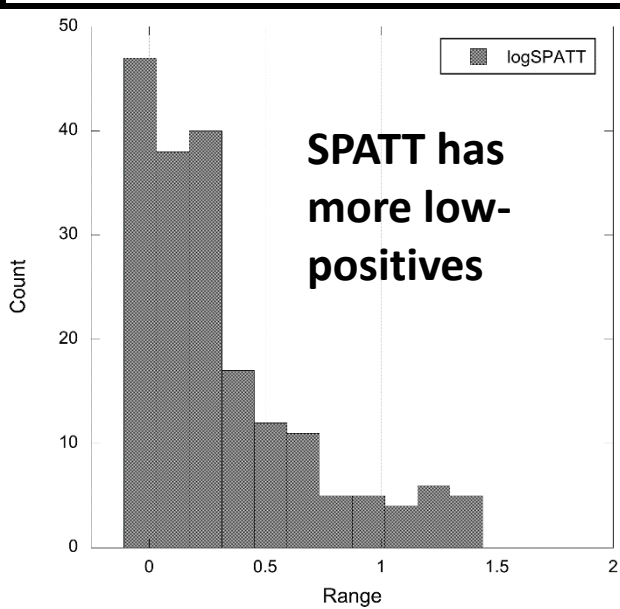
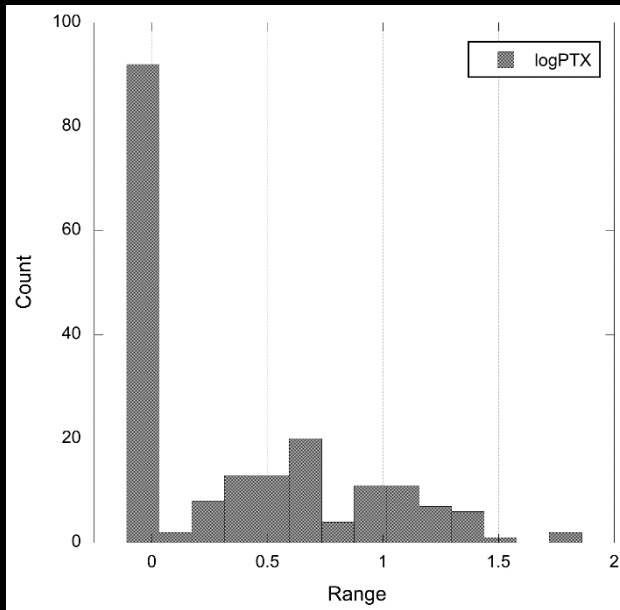
Microcystin Grab Sample (ppb)	SPATT (ng/g)
Non-Detect	5-13
< 1 ppb	10-50
1 < x < 10 ppb	50-200
> 10 ppb	175-275

Domoic Acid Mussel (ppm)	SPATT (ng/g)
0-5 ppm	0-30
5-10 ppm	30-50
10-20 ppm	50-75
>20 ppm	>150



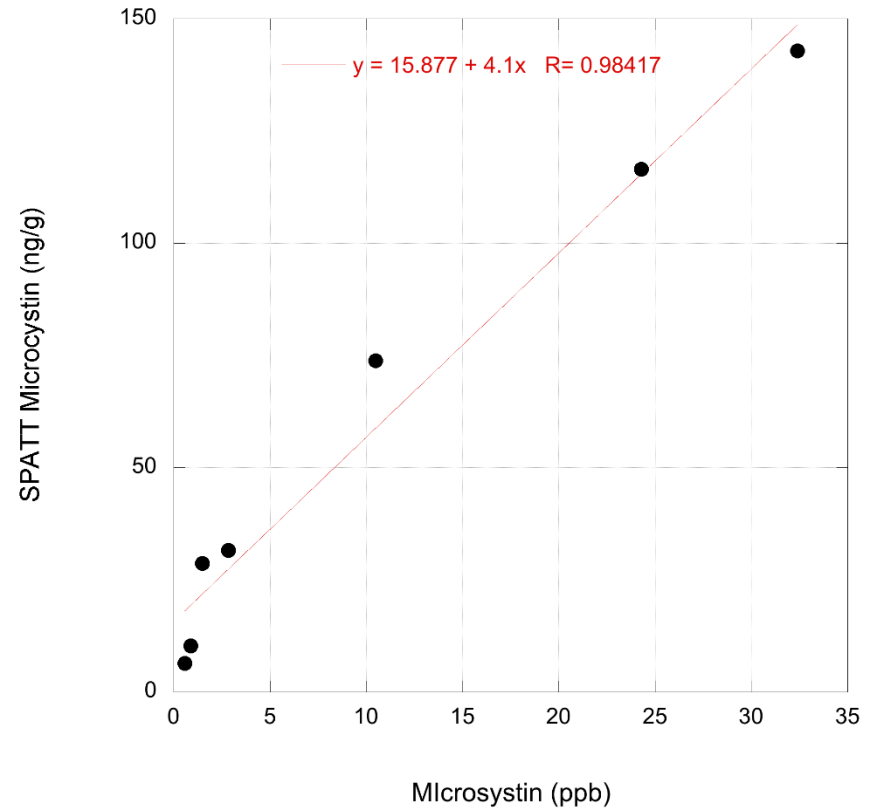
# SPATT vs. Grab Samples San Francisco Bay



# Adsorption Kinetics: Lab Trials

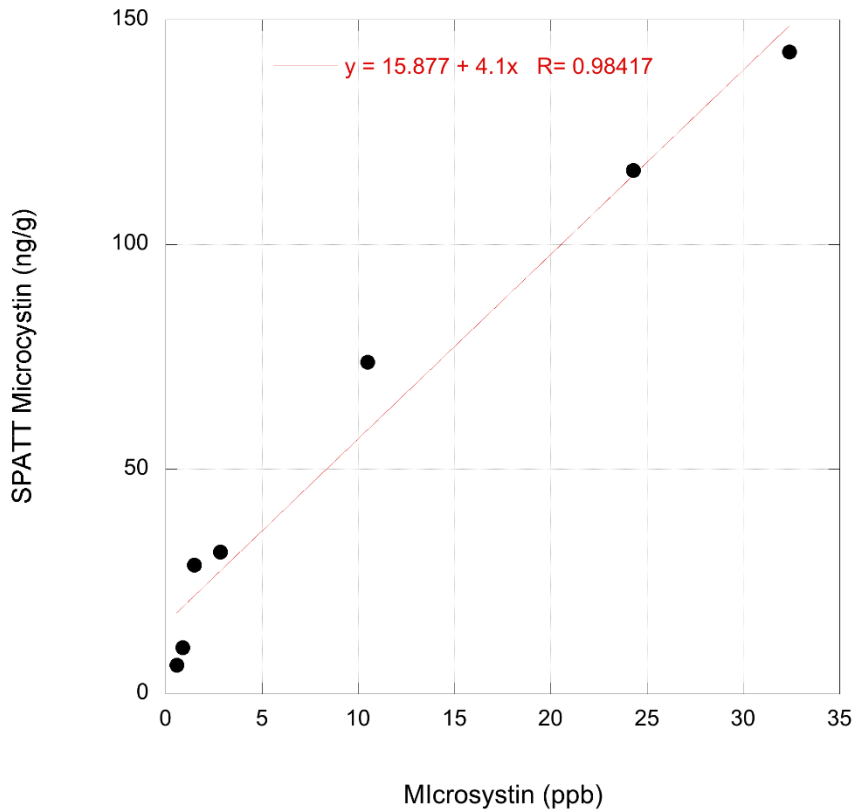


15-Minute Exposure

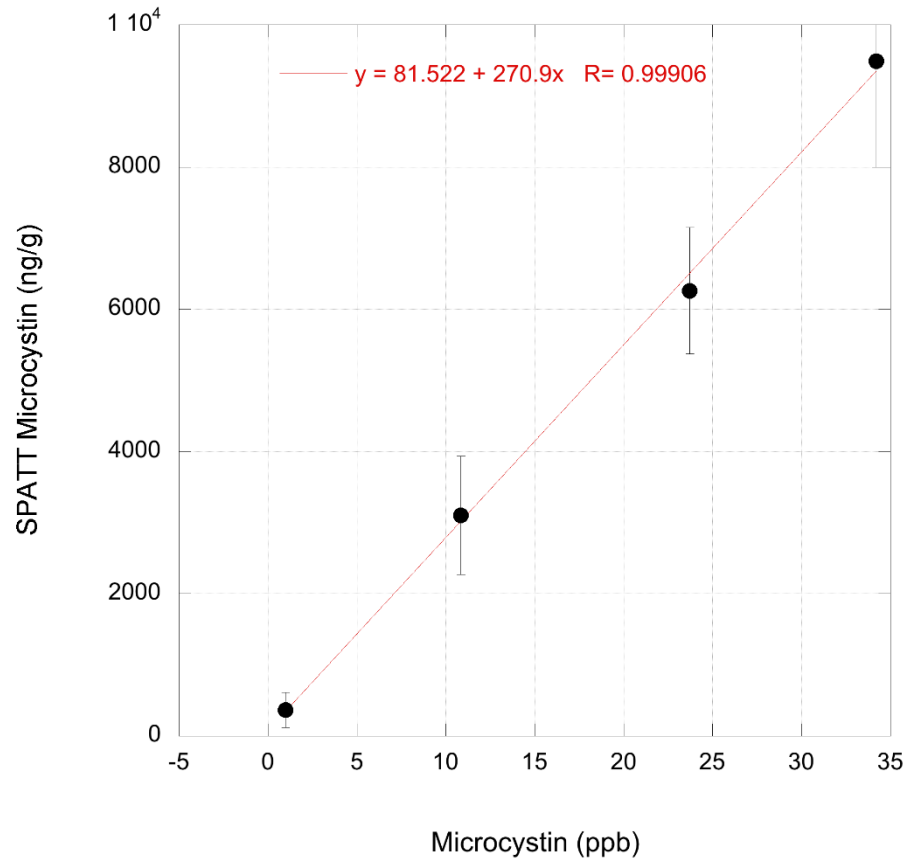


# Microcystins (time)

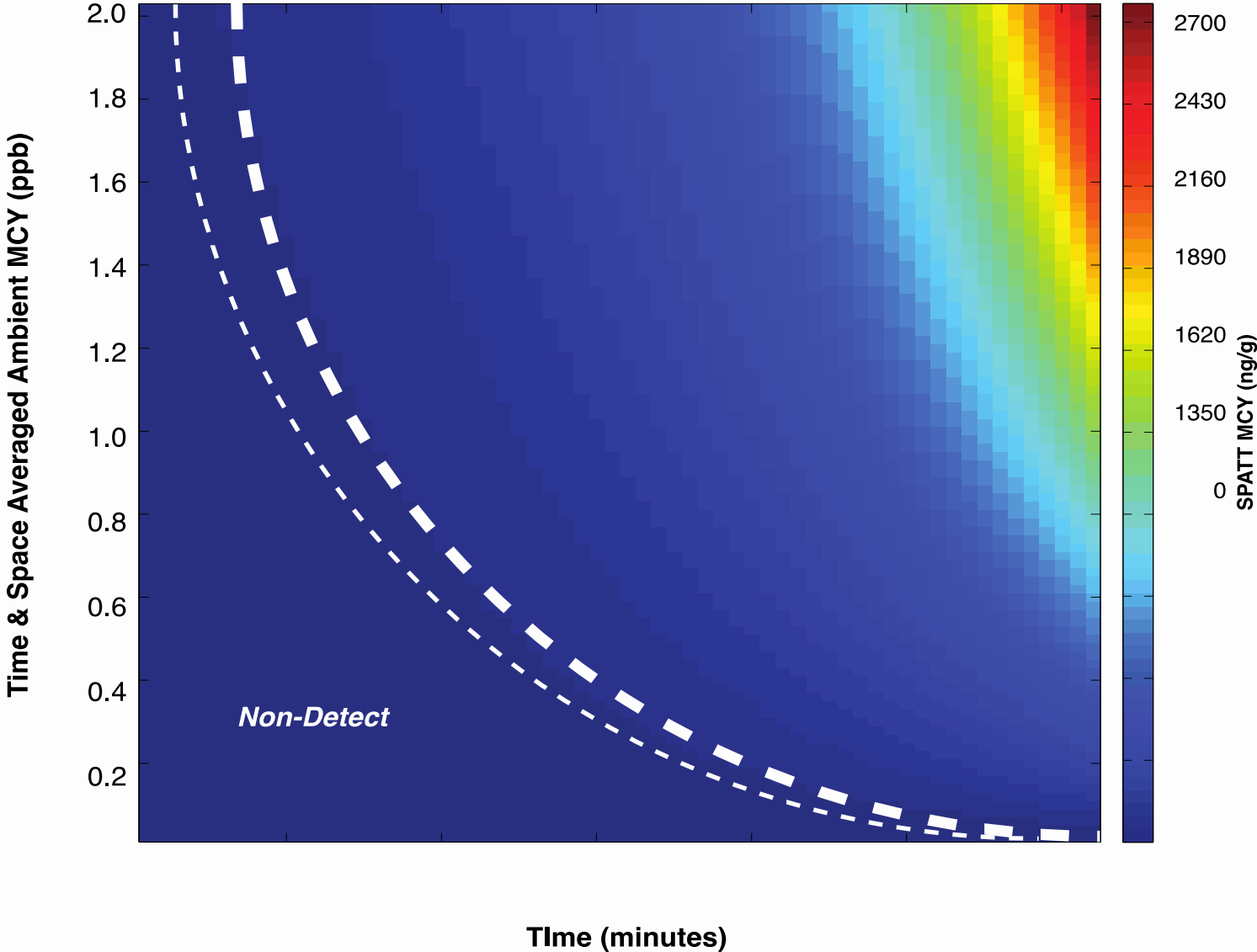
## 15 minute exposure



## 1 hour exposure



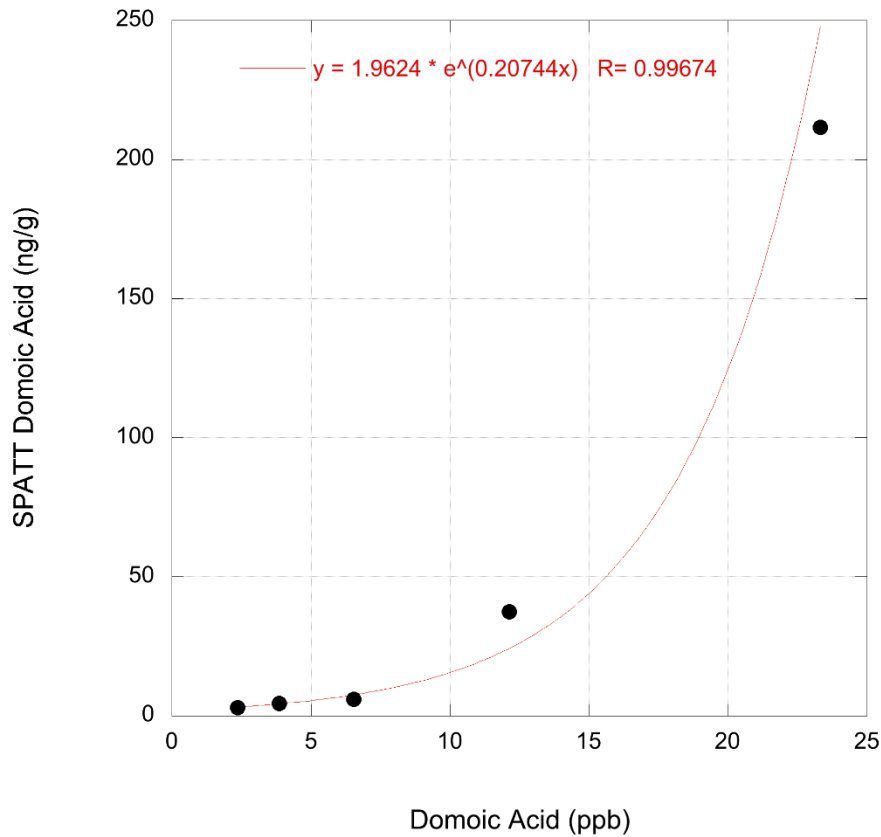
Because SPATT is time-averaging, increasing toxin (ng/g) is related to BOTH time of exposure and ambient concentration—it is helpful deploy SPATT *consistently*



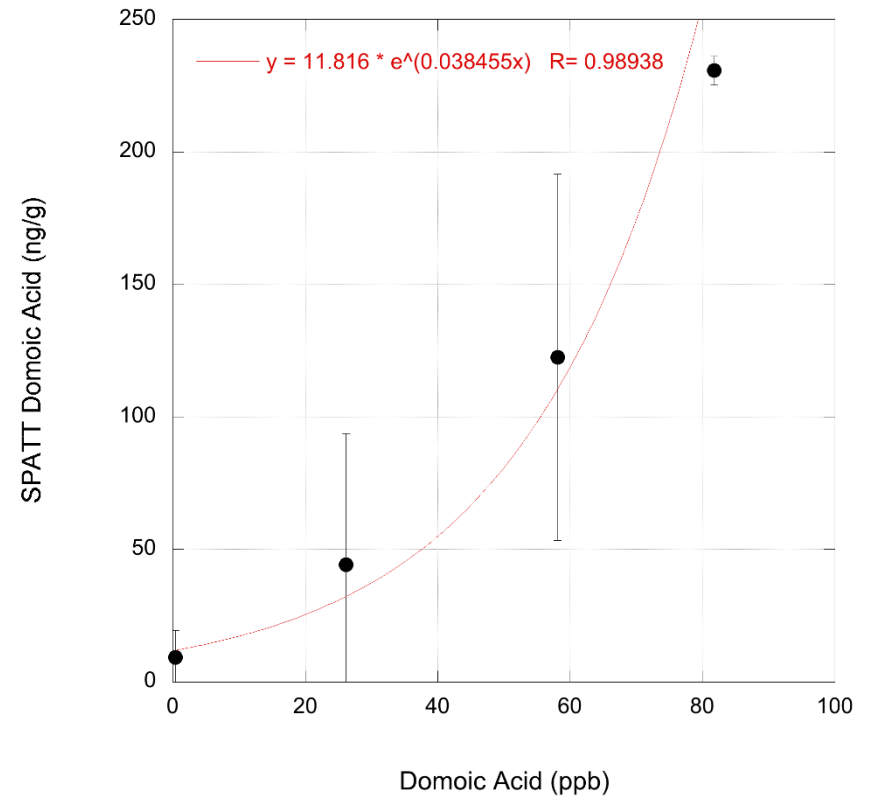
# Domoic Acid

(not as linear as MCY for HP20 resin; other resins are more linear)

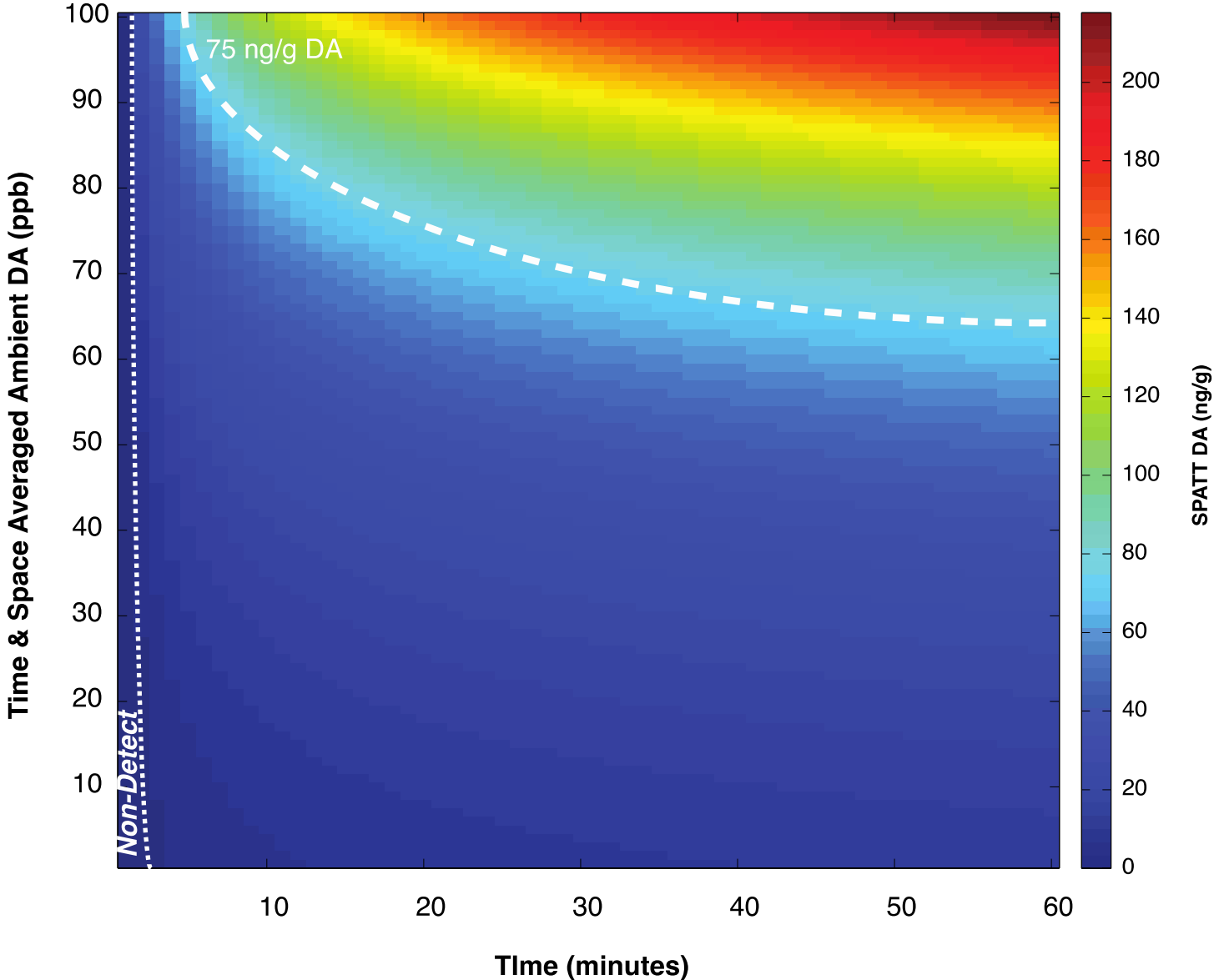
15 minutes



>20 hours



Because SPATT is time-averaging, increasing toxin (ng/g) is related to BOTH time of exposure and ambient concentration—it is helpful deploy SPATT *consistently*





# SPATT Availability

- Currently NOT commercially available as a pre-made unit
- Easy to make in the laboratory:
  - Lane et al., 2010: *Limnology & Oceanography: Methods*, 8: 645-660
  - Lane et al., 2012: ICHA14 Conference Proceedings, Crete 2010
  - Kudela, 2011: *Harmful Algae*, 11: 117-125
- Most commonly used resin is DIAON HP20 (widely applicable for many toxins)
- Compatible with standard analytical methods (LCMS, ELISA)

# Conclusions

- SPATT Advantages:

- Low cost, easy to deploy tool
- Applicable to marine, brackish and freshwater environments
- Measures marine and freshwater toxins
- Can be deployed in many different ways and in areas where there is limited sampling
- More robust indicator of toxin prevalence compared to grab samples ('snapshots')

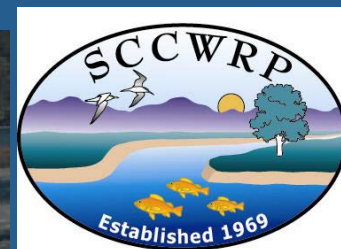
- Disadvantages:

- Cannot be directly compared to health advisory thresholds
  - However, SPATT concentrations of DA/MCY corresponding to matching mussel/water samples have been established

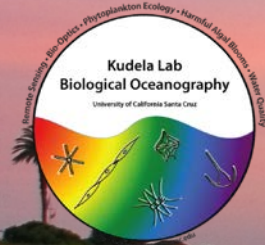
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# Thank You!



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