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

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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 *Pyrnmesium parvum*

**Central CA:**
- Lake Chabot: dog deaths
- Clear Lake: 16,000 μg/L
- East Bay Regional Parks: multiple lake closures
- SFB and Delta: multiple toxins ~year-round
- Pinto Lake: 2nd most toxic lake in the world; ongoing blooms; 1st closure

**Northern CA:**
- Klamath Basin: >10 years
- Trinity River: Anatoxin and Microcystins
- Russian and Eel Rivers: dog deaths

**Southern CA:**
- Lake Elsinore: Multiple toxins > health thresholds
- San Joaquin Marsh, 33,500 μg/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 µg/L
Scum: MCY 95,000 µg/L; CYL 181 µg/L; ANA 18.5 µg/L

Lake Chabot—11,000 µg/L; 800,000 µg/L scum

Pinto Lake—1,000 µg/L annually; 2.9 million µg/L scum

San Joaquin Marsh—33,500 µg/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'**

**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)
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
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)
  - Pectenotoxins (MacKenzie et al 2004, Fu et al 2009)
  - Saxitoxin (Lane et al 2010)
  - Spirolide toxins (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%

% of Toxic Sites: Depressional Wetlands

<table>
<thead>
<tr>
<th></th>
<th>Grab Samples</th>
<th>SPATT Samples</th>
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<tbody>
<tr>
<td></td>
<td>29%</td>
<td>83%</td>
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</table>

Howard et al., submitted
Microcystins Detected at Every Site Sampled

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

Grab Sample Results

SPATT Sample Results:
All sites toxic

Howard et al., submitted
Why Use SPATT?
Deploy In Areas with Limited Sampling

Site A
1 meter depth
1m Depth
Domoic Acid Saxitoxin Okadaic Acid
bd bd

Site B
7 meter depth
7m Depth
Domoic Acid Saxitoxin Okadaic Acid
bd bd

Pier:
DA below detection

Slide and data provided by Erica Seubert
SPATT Deployment: Buoy and Mooring

Map: Lucas and Kudela 2017; Buoy design George Robertson, Orange County Sanitation District
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

Why Use SPATT?
Uncovering Ubiquitous and Year Round Toxins
2011-2016: USGS Deployment of SPATT
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...
Particulate Domoic Acid

Pseudo-nitzschia spp.

North Central Bay South

Domoic Acid [ng/L]

0-5 5-25 25-100 100-200 200-400

Peacock et al. in prep
Dissolved Domoic Acid From SPATT

Peacock et al. in prep

Pseudo-nitzschia spp.
Particulate Microcystin

Microcystis spp.

North

Central Bay

South

Microcystin [ng/L]

Peacock et al. in prep
Dissolved Microcystin From SPATT

Microcystis spp.

North

Central Bay

South

Microcystin [ng/g]

- 0-2
- 2-4
- 4-6
- 6-8
- 8-10
- >10


Peacock et al. in prep
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
Domoic Acid in Mussels

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

Peacock et al. in prep
- Sometimes HIGH microcystin
- Variability
- No regulatory limit
- Are NOT monitored for

Regulatory Limit
Mean
< 5 ng/g
5 – 10 ng/g
> 10 ng/g

Gibble et al., 2016
PST in Mussels

- Can be marine or freshwater toxins
- Low but measurable

<10, 10-40, 40-80, >80 µg/100g

- April
- May
- June
- July
- August
- September
Okadaic Acid and DTX-2 in Mussels

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

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2010-2011 Monthly deployments 2011-2013 Weekly deployments

Gibble and Kudela, 2014
SPATT Deployment: AUVs

Liquid Robotics G5 surface wave glider

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

Beldalet et al., 2014

Photo: http://gliders.oceantrack.org/
SPATT Deployment: AUVs

Teledyne Webb Slocum Gliders

SPATT detected domoic acid, saxitoxin; no okadaic acid detected

Slide courtesy of Erica Seubert and David Caron
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.

<table>
<thead>
<tr>
<th>Microcystin Grab Sample (ppb)</th>
<th>SPATT (ng/g)</th>
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<tbody>
<tr>
<td>Non-Detect</td>
<td>5-13</td>
</tr>
<tr>
<td>&lt; 1 ppb</td>
<td>10-50</td>
</tr>
<tr>
<td>1 &lt; x &lt; 10 ppb</td>
<td>50-200</td>
</tr>
<tr>
<td>&gt; 10 ppb</td>
<td>175-275</td>
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<table>
<thead>
<tr>
<th>Domoic Acid Mussel (ppm)</th>
<th>SPATT (ng/g)</th>
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<tbody>
<tr>
<td>0-5 ppm</td>
<td>0-30</td>
</tr>
<tr>
<td>5-10 ppm</td>
<td>30-50</td>
</tr>
<tr>
<td>10-20 ppm</td>
<td>50-75</td>
</tr>
<tr>
<td>&gt;20 ppm</td>
<td>&gt;150</td>
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SPATT vs. Grab Samples San Francisco Bay

SPATT has more low-positives.
Adsorption Kinetics: Lab Trials

15-Minute Exposure

y = 15.877 + 4.1x  R= 0.98417
Microcystins (time)

15 minute exposure

\[ y = 15.877 + 4.1x \quad R = 0.98417 \]

1 hour exposure

\[ y = 81.522 + 270.9x \quad R = 0.99906 \]
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

\[ y = 1.9624 \times e^{0.20744x} \quad R = 0.99674 \]

>20 hours

\[ y = 11.816 \times e^{0.038455x} \quad R = 0.98938 \]
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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