Cyanotoxin Monitoring with SPATT Passive Samplers in Northern California Rivers, 2019

December 2022

Freshwater Harmful Algal Bloom (FHAB) Monitoring and Response Program
California North Coast Regional Water Quality Control Board
5550 Skylane Boulevard, Suite A
Santa Rosa, CA 95403
http://www.waterboards.ca.gov/northcoast

SWAMP-MR-RB1-2022-0002

List of Authors

Rich Fadness[1]
Michael Thomas[1]
Keith Bouma-Gregson[2, *]

1. North Coast Regional Water Quality Control Board
   5550 Skylane Boulevard, Suite A
   Santa Rosa, CA 95403

2. State Water Resources Control Board
   Office of Information Management and Analysis
   1001 I Street
   Sacramento, CA 95814

* Current address:
  U.S. Geological Survey
  California Water Science Center
  6000 J Street, Placer Hall
  Sacramento, CA 95819

With assistance from Katharine Carter, North Coast Regional Water Quality Control Board Adaptive Management Unit, and Alydda Mangelsdorf, North Coast Regional Water Quality Control Board Planning and Watershed Stewardship Division.

This report should be cited as follows:

NCRWQCB 2022. Cyanotoxin Monitoring with SPATT Passive Samplers in Northern California Rivers, 2019. Freshwater Harmful Algal Bloom Monitoring and Response Program, North Coast Regional Water Quality Control Board, Santa Rosa, CA.

List of Acronyms

ATX	Anatoxins
CCHAB	California Cyanobacteria and Harmful Algal Bloom Network
CyanoHAB	Cyanobacteria Harmful Algal Bloom
CYN	Cylindrospermopsins
ELISA	Enzyme-Linked Immunosorbent Assay
FHAB	Freshwater Harmful Algal Bloom
HAB	Harmful Algal Bloom
LCMS	Liquid Chromatograph with Mass Spectrometry
MCY	Microcystins
MQO	Measurement Quality Objective
NCRWQCB	North Coast Regional Water Quality Control Board
NOD	Nodularins
OEHHA	Office of Environmental Health Hazard Assessment
SOP	Standard Operating Procedure
SPATT	Solid Phase Adsorption Toxin Tracking
STX	Saxitoxins

Glossary

Benthic – refers to organisms that attach to the bottom substrates of rivers or other waterbodies.

Benthic mats – cyanobacteria that are attached to, or have at one point been attached to, the stream bottom, in contrast to planktonic cyanobacteria, which are free-floating in the water column.

Congener – cyanotoxin molecule with minor molecular variation on the same general molecular structure. Cyanotoxin classes can contain multiple congeners (e.g., microcystins).

Cyanobacteria – historically referred to as “blue-green” algae, they are actually bacteria (i.e., prokaryotes) that contain chlorophyll-a and are capable of photosynthesis. Cyanobacteria co-occur with “true” algae (i.e., eukaryotes).

Cyanotoxins – toxic molecules produced by cyanobacteria that through contact can affect the skin (i.e., dermatoxins), or through ingestion can affect the liver (i.e., hepatotoxins) and central nervous system (i.e., neurotoxins).

Enzyme-linked immunosorbent assay (ELISA) – laboratory method for detecting and quantifying cyanotoxins by reacting proteins and antibodies then measuring color change in plate wells. ELISA can measure multiple cyanotoxin congeners.

Harmful algal blooms (HABs) – a “bloom” is a rapid proliferation of algae and/or cyanobacteria. HABs refer to blooms of cyanobacterial species that can produce toxins that are harmful to humans and wildlife.

Liquid chromatography with mass spectrometry (LCMS) – laboratory method for detecting and quantifying cyanotoxins by separating and detecting charged ions then identifying types of molecules in a sample. LCMS can only measure specific congeners that have a known standard.

Reach – delineated linear segment of a stream or river where monitoring and sampling occurs.

Solid phase adsorption toxin tracking (SPATT) – passive samplers constructed of an inert mesh and filled with porous resin capable of adsorbing cyanotoxins.

Substrate – solid surface to which organisms can attach; in a streambed it includes both inorganic (e.g., cobbles) and organic (e.g., plants or wood) surfaces.

Contents

Figures

Tables

Appendices

1 Introduction

1.1 Study Rational and Objectives

This special study evaluated the performance of Solid Phase Adsorption Toxin Tracking (SPATT) samplers that adsorb and desorb dissolved cyanotoxins released from benthic cyanobacteria into the water column of rivers. The results of this study are intended to inform waterbody managers and public health officials on how to utilize this monitoring tool to inform decisions and appropriate response actions for the protection of the recreating public and pets from benthic cyanobacteria and their cyanotoxins.

Monitoring sites were established in three rivers with a history of benthic cyanobacterial blooms: the Navarro River, Russian River, and South Fork Eel River (Puschner et al. 2008, Bouma-Gregson et al. 2018, Conklin et al. 2020, NCRWQCB 2022). SPATTs were deployed at varying consecutive and concurrent time intervals in two separate experiments to determine how samplers adsorb and desorb cyanotoxins over time. The goal of this study was to determine an appropriate deployment length for SPATT samplers in a natural setting to provide guidance on the development of a monitoring program utilizing SPATTs to detect cyanotoxins. Additionally, SPATTs were constructed of two different commercially available resins to better understand the adsorption performance of each.

1.2 Cyanobacteria and Cyanotoxin Overview

Cyanobacteria can synthesize many types of toxic molecules, collectively known as cyanotoxins, that are harmful to humans and animals (Dittmann et al. 2013). In freshwater, cyanobacteria can form dense blooms, commonly called cyanobacteria harmful algal blooms (cyanoHABs), which can lead to high cyanotoxin concentrations and impaired water quality (Huisman et al. 2018). Planktonic blooms, or floating blooms that generally occur in lakes, produce cyanotoxins within small cyanobacterial cells or colonies that grow suspended in the water column and near the water surface. Benthic blooms, or cyanobacteria that grow as mats attached to bottom surfaces such as sediment, cobbles, and macrophytes in rivers (Quiblier et al. 2013, Wood et al. 2020), produce cyanotoxins within a cohesive mat matrix. Both bloom types can release dissolved cyanotoxins into the water column (extracellular) but cyanotoxin concentrations are highest within cyanobacterial cells (intracellular). Cyanotoxin concentrations do not always correlate with cyanobacteria density because not all cyanobacteria strains produce cyanotoxins.

Although cyanotoxins have diverse chemical structures, they generally affect the nervous system (neurotoxins), liver (hepatotoxins), skin (dermatoxins), and sometimes kidneys (nephrotoxins). Cyanotoxin production varies among cyanobacterial genera, and the function of cyanotoxins within cyanobacterial cells is still not clearly understood (Huisman et al., 2018). A previous study by the North Coast Regional Water Quality Control Board (Regional Water Board) documented that anatoxins, microcystins, and nodularins are commonly found in benthic cyanobacteria in northern California rivers

(NCRWQCB 2022); these cyanotoxins, their mode of action, and health effects are shown in Table 1.

Table 1. Cyanotoxins evaluated in this special study by the Regional Water Board.

Toxin Class	Toxin Type	Acute Health Effects*
Anatoxins (ATX)	Neurotoxin	Tingling, burning, numbness, drowsiness, incoherent speech, salivation, respiratory paralysis leading to death.
Microcystins (MCY)	Hepatotoxin	Liver damage, abdominal pain, headache, sore throat, vomiting and nausea, dry cough, diarrhea, blistering around the mouth, and pneumonia.
Nodularins (NOD)		

*See Chorus and Welker 2021 for more information on health effects.

In rivers, benthic mat-forming cyanobacteria occupy many ecological niches. Their distribution can be sporadic, patchy, or cover large areas that may dominate large portions of the riverbed. In some instances, a river reach may contain numerous habitats containing dozens of toxigenic cyanobacterial species with the potential to produce several cyanotoxins at the same time. The timing of mat growth varies from year to year and species to species, though mat growth and expansion generally occurs over weeks to months, and mats can persist throughout the summer growing season, generally June through October (Bouma-Gregson et al., 2018; McAllister et al., 2018; Thomson-Laing et al., 2021; NCRWQCB 2022). Cyanobacterial mats usually dissipate with changing environmental conditions such as the onset of winter when temperatures cool and higher flows mobilize stream sediment and slough the benthic biomass. Detecting and tracking cyanotoxins from benthic cyanobacteria can be challenging due to the diverse assemblage of strains forming a benthic bloom, the variable timespans of blooms, and changing densities due to environmental conditions.

1.3 Passive Sampler Overview

Solid Phase Adsorption Toxin Trackers (SPATTs) are a type of passive sampler that can be used to monitor dissolved toxins (MacKenzie et al. 2004). SPATTs are “teabag-like” samplers constructed of an inert mesh filled with porous resin. When deployed into a waterbody, SPATTs adsorb dissolved cyanotoxins onto the sampler resin (Kudela 2017; Roue et al. 2018). The amount of cyanotoxins increases on the sampler until equilibrium is reached with the surrounding water. Conversely molecules may desorb and be released back into the water column in response to water column concentration fluctuations. Because SPATTs can be left in the water for hours to days, they can integrate cyanotoxins over time and potentially detect concentrations that would not be captured using discrete water grab samples. In flowing systems such as rivers, SPATTs are particularly relevant as it can be difficult to measure fluctuations or pulses of cyanotoxin concentrations flowing downstream with only discrete water grab samples (Wood et al. 2011, 2018).

While passive samplers are attractive for their simplicity and deployment ease, interpreting data from field deployed SPATTs can be challenging. Recent research provides recommendations on SPATT deployment and data interpretation under laboratory conditions with controlled cyanotoxin concentrations (Kudela 2020), however, little is known about how in-situ environmental conditions impact adsorption-desorption kinetics. The deployment length for SPATT samplers in a field setting also remains poorly understood since it is difficult to know whether different SPATT concentrations are due to adsorption performance or truly different cyanotoxin concentrations in the water column and among sampling events. Given the objective of this special study (see Section 1.1), SPATTs were deployed consecutively and concurrently in the field for differing lengths of time to evaluate the impact of deployment length on cyanotoxin concentrations. Deployment length was evaluated in two separate experiments in which some SPATTs were replicated to determine variation among samplers that were deployed at the same location. Additionally, SPATTs were constructed of two different commercially available resins to better understand the adsorption performance of each.

1.4 Watershed Description

The Regional Water Board conducted this special study in the Navarro, Russian, and South Fork Eel Rivers as part of a larger monitoring effort that evaluated benthic cyanobacteria and their cyanotoxins in the North Coast Region. A brief description of each watershed is included below. More information can be found in Benthic Cyanobacteria and Cyanotoxin Monitoring in Northern California Rivers, 2016-2019 (NCRWQCB 2022).

1.4.1 Navarro River Watershed

The Navarro River is a 315 mi^2 coastal watershed in southern Mendocino County, approximately 120 miles north northwest of San Francisco, 30 miles west of Ukiah, and three miles south of the town of Albion. Elevations in the basin range from sea level to about 3,000 feet. State Highway 128 traverses much of the watershed, paralleling Rancheria Creek and the mainstem Navarro River for approximately 25 miles. The Navarro River flows through the Coast Ranges, and Anderson Valley, and out to the Pacific Ocean at Mendocino Coast State Seashore. Rainfall averages about 40 inches per year in the center of the watershed at Philo, with most of it occurring between December and March.

1.4.2 Russian River Watershed

The Russian River is a 1,485 mi^2 watershed located in Sonoma and southern Mendocino counties with elevation that ranges from sea level to 4,300 feet. The Russian River flows southward for nearly 110 river miles from its headwaters north of Ukiah in Mendocino County, along US Highway 101, through several alluvial valleys before turning west for the last 30 miles and entering the Pacific Ocean at Jenner in Sonoma County.

The Russian River is a highly regulated river with two large dam impoundments on two primary tributaries and several seasonal summer dams on the river's mainstem. The impoundments modify the natural flows of the river by decreasing the high flows of winter and increasing the low flows of summer. Except for large storm events, the flows in the upper Russian River are dominated by releases from Lake Mendocino and those of the lower Russian River are generally increased with the addition of outflow from Lake Sonoma.

The Russian River is heavily recreated with many access points along its length. The summertime reservoir releases provide sufficient flows for recreational activities and the distribution of drinking water within Mendocino, Sonoma, and Marin Counties. Several recreational summer dams and periodic closures of the river's mouth turn the lower sections of the Russian River into a series of shallow ponded sections connected by short free-flowing river segments. The summer seasonal flows remain relatively consistent throughout the summer season and year to year, providing a stable flow regime that allows for various ecological niches to develop within the river where benthic algae and cyanobacteria can establish and flourish.

1.4.3 South Fork Eel River Watershed

The South Fork Eel River is a 688 mi^2 watershed located in northern Mendocino and southern Humboldt Counties, with elevations that range from 100 to 4,500 feet. The South Fork Eel River flows northward for approximately 100 river miles from the headwaters in the Laytonville area in Mendocino County, along US Highway 101, through Humboldt Redwoods State Park in Humboldt County, and finally joins the mainstem Eel River upstream of the town of Weott, approximately 40 river miles from the Pacific Ocean. Like the mainstem Eel River, the South Fork Eel River is heavily recreated with many access points along its length.

The South Fork Eel River is a free-flowing river with no impoundments. The unregulated flows reflect the seasonality of the precipitation record with higher runoff flows in the winter and low base flows in the summer months.

2 Methods

2.1 Sampling Locations

Two experiments were conducted at a total of five sites during 2019. One experiment included SPATTs deployed over a 4-day period and the other experiment included SPATTs deployed over a 14-day period. Sampling sites in the Navarro, Russian, and South Fork Eel Rivers were opportunistically selected from a larger monitoring effort that evaluated cyanobacteria and their cyanotoxins in the North Coast Region (Table 2, Figure 1). Sites were selected from locations where exploratory SPATT samplers documented cyanotoxins. Of these locations, one site was selected for each of the Navarro and Russian Rivers. In the South Fork Eel River, three sites were selected and

spaced roughly 20 rivers miles apart. Depending on the site, SPATTs were deployed in the rivers as part of a 4-day or 14-day experiment during the 2019 season. The 4-day experiment included concurrent and consecutive samplers that were deployed from one to four days in length, while the deployment lengths in the 14-day experiment ranged from two to 14 days. See *Sampling Design and Rationale* for more information on experimental design.

Table 2. Sampling sites in the Navarro, Russian, and South Fork Eel Rivers, 2019.

Site Code	Site Name	Latitude	Longitude	SPATT Experiment	
				4-day	14-day
113NA9990	Navarro River above Indian Creek	39.05711	-123.44180	August	---
111SF6856	South Fork Eel River at Big Bend Lodge	38.82546	-123.68069	August	---
111SF4640	South Fork Eel River at Cooks Valley	40.00004	-123.78687	August	Sep-Oct
111SF2423	South Fork Eel River below Dean Creek	40.16140	-123.79155	August	---
114RR5407	Russian River at Cloverdale Airport	38.77386	-123.98807	---	Sep-Oct

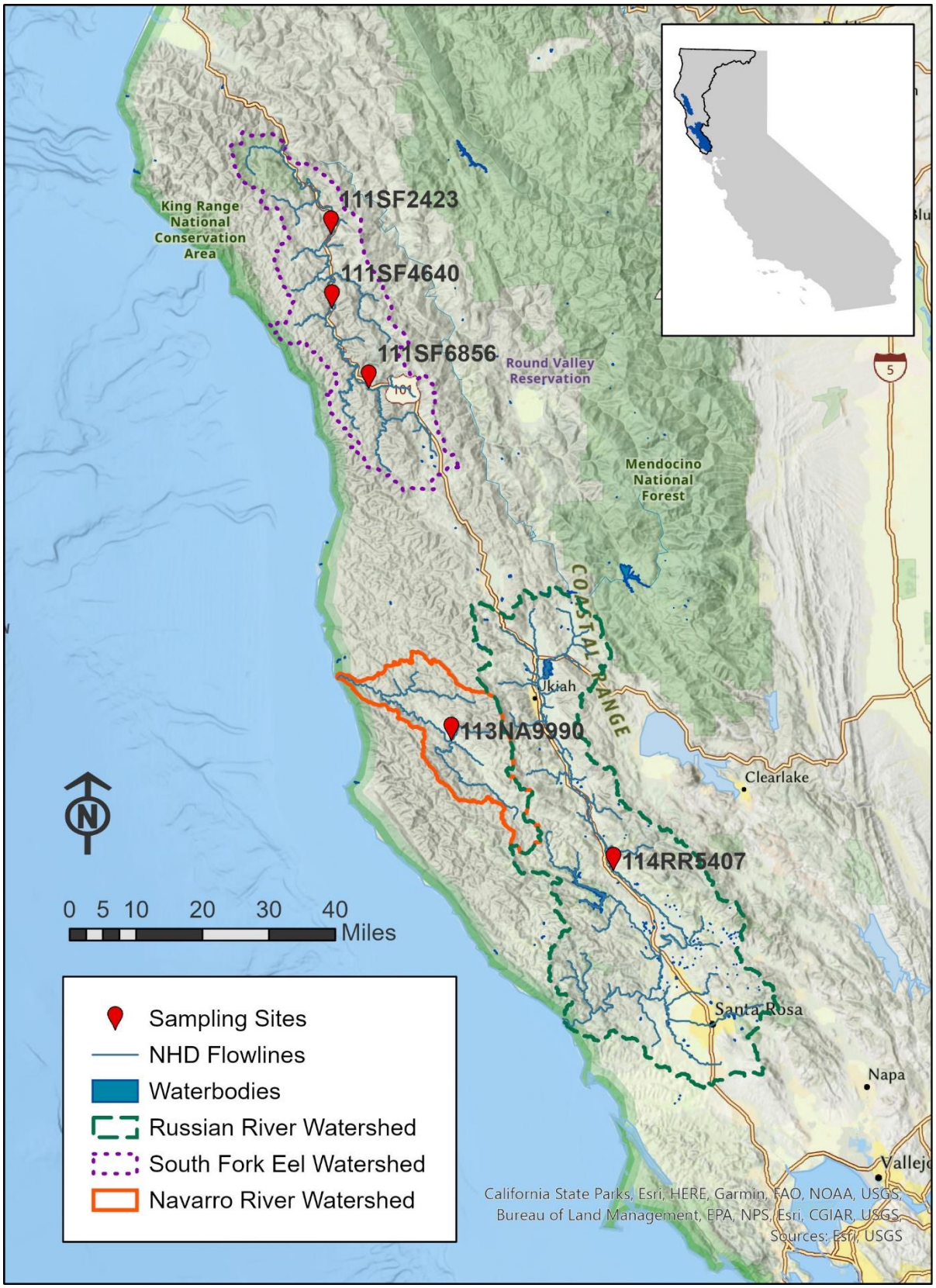

Figure 1. Map of the sampling sites in the Navarro, Russian, and South Fork Eel Rivers.

2.2 Field Sampling

2.2.1 SPATT Passive Samplers

SPATT samplers were constructed by placing 3.0 grams (g) of resin onto a 10 centimeter (cm) wide square of 100 µm Nitex cloth. A second square of Nitex was placed on top of the resin and both cloths were clipped into a 6.3 cm diameter embroidery hoop ring to create the sampler. Samplers were submerged in 100% methanol for 24 hours to clean the resin immediately after construction. Samplers were then rinsed with Milli-Q water and stored in plastic bags with 20-50 milliliters (mL) of Milli-Q water at 4ºC in the dark until deployment.

A variety of resins are commercially available for SPATT sampler construction, including HP20 and HLB resins, which were used in this special study. HP20 is a macroporous styrenic polymeric bead type resin used for adsorption/desorption process scale applications. HP20 is produced by Diaion® and is available through Sorbent Technologies, Inc. HLB resin is a co-polymer of divinybenzene and vinyl pyrrolidinone that act as imbedded hydrophilic groups that retain polar analytes. HLB is available through Oasis®. HP20 is considered a “universal” resin in that it captures a variety of freshwater and marine toxins, however, HLB was shown to have higher adsorption/desorption rates, sensitivity, and maximum capacity under laboratory conditions (Kudela 2017, 2020). Kudela (2020) also demonstrated that HLB may be more sensitive in the field, though differences were not considerable enough to recommend HLB over HP20. For the 4-day experiment, all SPATT samplers were constructed with HP20 resin. To assess differences in resin performance, the 14-day experiment included an equal number of SPATTs with HP20 resin (N=22) and HLB resin (N=22) for each river. See *Sampling Design and Rationale* for more information on experimental design.

SPATT samplers were deployed in accordance with *Standard Operating Procedure for SPATT Assemblage and Extraction of HAB Toxins* (Howard et al., 2018). Using zip ties, samplers were attached to chains that were strung between metal stakes in well-mixed zones within the sample reach (Figure 2). SPATTs were deployed mid-depth in locations with enough flow velocity to generate well-mixed water, but not enough velocity to damage the experimental set up. Individual samplers were randomly assigned to a deployment group ranging from one to 14 days in length.

Figure 2. Photograph of SPATTs deployed in the South Fork Eel River, 2019.

Upon retrieval, SPATTs were stored at 4-6° C in the dark and delivered to the laboratory for analysis within 48 hours of sample collection. Any collected SPATTs exceeding a 48-hour hold time were stored at -20° C and shipped frozen for overnight delivery. Cyanotoxins were extracted from SPATTs following methods in Kudela (2011) and Gibble and Kudela (2014). SPATT samplers were thawed, and the resin rinsed with Milli-Q water. The resin was poured into a disposable liquid chromatography column and placed on a vacuum manifold. Cyanotoxins were extracted from the resin with consecutive 10-, 20-, and 20-mL rinses of 50% solution of 100% methanol and Milli-Q water. The concentration of cyanotoxins in each extract were summed and the final result reported as mass of cyanotoxin per mass of resin (ng/g).

2.2.2 Ambient Water Column Grab Samples

Ambient water column grab samples provide discrete measures of cyanotoxin concentrations at the time and location the sample is collected, measuring both the dissolved cyanotoxin fractions in the water column and any particulate (i.e., floating or suspended cyanobacterial cells) that may be present. Grab samples were collected to determine instantaneous cyanotoxin concentrations during the 4-day experiment only.

Sample collection followed California's Surface Water Ambient Monitoring Program (SWAMP) standard operating procedures (SOPs) for harmful algal blooms (SWAMP 2017a). All water column samples were collected from well-mixed areas within the sampling reach. Samples were stored at 4-6° C and delivered to the laboratory for

analysis within 48 hours of sample collection. Any collected samples exceeding a 48-hour hold time were stored at -20° C and shipped frozen for overnight delivery.

2.3 Sampling Design and Rationale

This special study includes separate 4-day and 14-day in-situ experiments carried out during different time periods in the summer and fall of 2019. Each experimental design is described separately in the following sections.

2.3.1 4-Day Experimental Design

SPATT samplers were deployed over four days from August 26-30, 2019, at three sites in the South Fork Eel River and one site in the Navarro River (Table 2). In the 4-day experiment, HP20 resin was used for all samplers. A total of 46 SPATTs were deployed among the 4 sites for one to four days to create a continuous time series (Figure 3). This deployment schedule generated eight unique deployment length and experiment day treatments. The deployment groups follow an alphanumeric naming convention where the number indicates deployment length (i.e., number of experiment days), and the letter represents when samplers were deployed in alphabetical order.

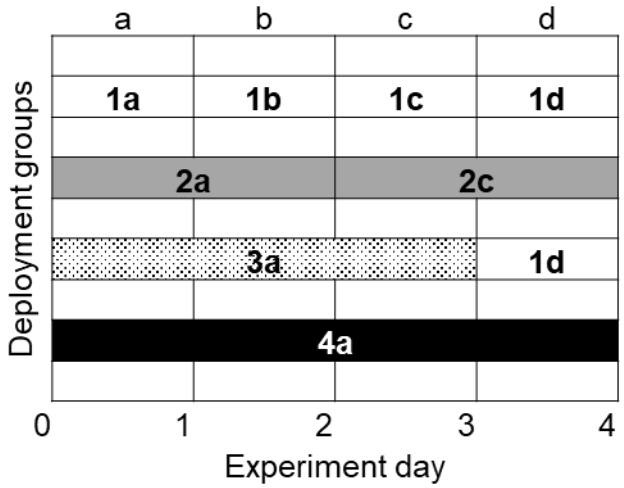

Figure 3. Diagram showing different SPATT deployment groups for the 4-day in-situ SPATT experiment in the Navarro and South Fork Eel Rivers, 2019. Numbers represent deployment length and letters represent when samples were deployed. Vertical lines indicate days when samplers were retrieved and deployed.

The deployment schedule allowed for the comparison of samplers deployed consecutively and concurrently but for different lengths of time. For example, two samplers were deployed on day zero (2a and 4a), one sampler was retrieved on day two (2a) with a new sampler (2c) immediately deployed. Then on day four, both in-stream samplers (2c and 4a) were retrieved. As a result, cyanotoxin concentrations of the 0–2-day sampler (2a) and the consecutive 2-4-day sampler (2c) could be compared

to the concurrent 0–4-day sampler (4a). Depending on the site and deployment date, some deployment groups were either duplicated or triplicated to evaluate variation and repeatability (Table 3).

Table 3. Deployment groups and replication of SPATT samplers deployed concurrently during the 4-day in-situ experiments in the Navarro and South Fork Eel Rivers, 2019.

River	Site	Concurrent Deployments	Deployment Days for each SPATT and Number of Replicates (N) *
Navarro	113NA9990	1a-1b-1c-1d	$1_{(1)}$-$1_{(1)}$-$1_{(2)}$-$1_{(1)}$
		2a-2c	$2_{(1)}$-$2_{(3)}$
		3a-1d	$3_{(1)}$-$1_{(1)}$
		4a	$4_{(3)}$
South Fork Eel	111SF2423	1a-1b-1c-1d	$1_{(1)}$-$1_{(1)}$-$1_{(1)}$-$1_{(1)}$
		2a-2c	$2_{(3)}$-$2_{(1)}$
		3a-1d	$3_{(1)}$-$1_{(1)}$
		4a	$4_{(3)}$
	111SF4640	1a-1b-1c-1d	$1_{(2)}$-$1_{(1)}$-$1_{(2)}$-$1_{(1)}$
		2a-2c	$2_{(1)}$-$2_{(2)}$
		3a-1d	$3_{(1)}$-$1_{(1)}$
		4a	$4_{(3)}$
	111SF6856	1a-1b-1c-1d	$1_{(1)}$-$1_{(1)}$-$1_{(1)}$-$1_{(1)}$
		2a-2c	$2_{(1)}$-$2_{(1)}$
		3a-1d	$3_{(1)}$-$1_{(1)}$
		4a	$4_{(1)}$

*Deployment day is the large number followed by the number of replicates in parenthetical subscript. For example, $4_{(2)}$ means a sampler was deployed for four days and duplicated, and $2_{(3)}$ means a sampler was deployed for two days and triplicated.

2.3.2 14-Day Experimental Design

SPATT samplers were deployed over 14 days from September 27-October 11, 2019, at one site in the Russian River and one site in the South Fork Eel River. For this experiment, HLB and HP20 resins were used to compare their adsorption and desorption performance. SPATTs for each resin type were paired and subject to the same deployment groups for each river. Length of deployment for each sampler ranged from two to 14 days and a total number of 44 SPATTs (22 per resin type) were deployed and retrieved in each river to create a continuous time series. This schedule generated 12 unique deployment length and experiment day combinations for each river (Figure 4). The deployment groups follow an alphanumeric naming convention where the number indicates deployment length (i.e., number of experiment days), and the letter represents when samplers were deployed in alphabetical order.

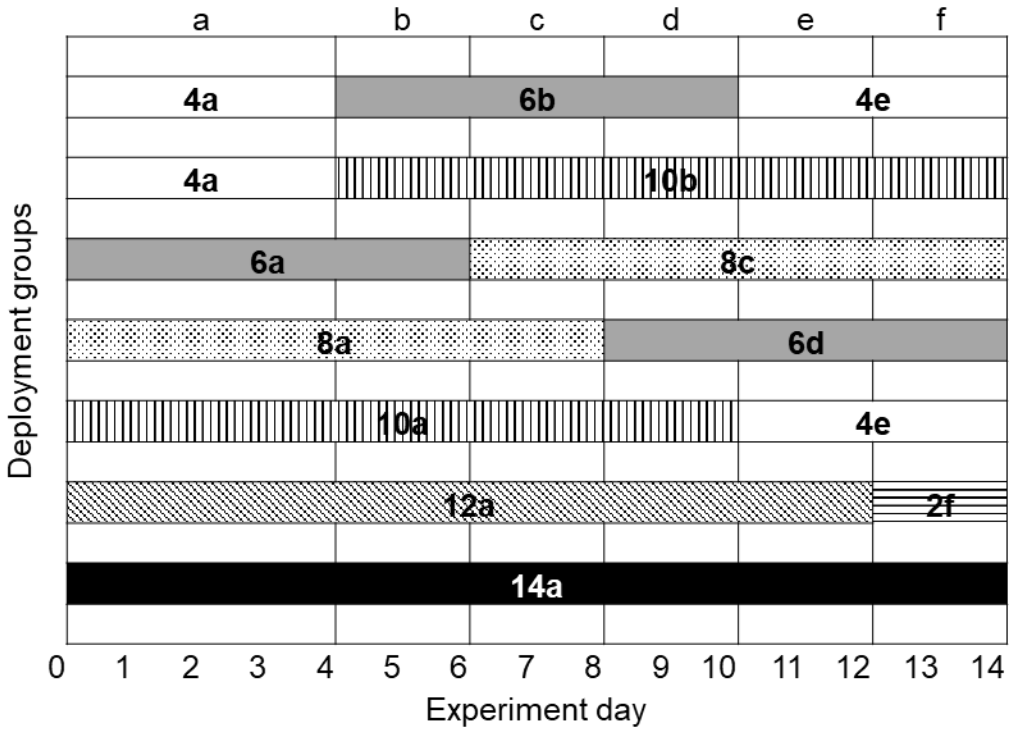

Figure 4. Diagram showing different SPATT deployment groups for the 14-day in-situ SPATT experiment in the Russian and South Fork Eel Rivers, 2019. Numbers represent deployment length and letters represent when samples were deployed. Vertical lines indicate days when samplers were retrieved and deployed.

As with the 4-day experiment, the deployment schedule for the 14-day experiment allowed for the comparison of samplers deployed consecutively and concurrently but for different lengths of time. For example, two samplers were deployed on day zero (6a and 14a), one sampler was retrieved on day six (6a) with a new sampler (8c) immediately deployed. Then on day 14, both in-stream samplers (8c and 14a) were retrieved. As a result, cyanotoxin concentrations of the 0–6-day sampler (6a) and the consecutive 6–14-day sampler (8c) could be compared to the concurrent 0–14-day sampler (14a). For each resin type and river, triplicate SPATT samplers were deployed at five deployment lengths to investigate variation and repeatability (Table 4).

Table 4. Deployment groups and replication for SPATT samplers deployed concurrently during the 14-day in-situ experiments in the Russian and South Fork Eel Rivers, 2019.

River	Site Code	Concurrent Deployments	Deployment Days for each SPATT and Number of Replicates (N) *
Russian	114RR5407	4a-6b-4e	$4_{(1)}$-$6_{(3)}$-$4_{(1)}$
		4a-10b	$4_{(1)}$-$10_{(1)}$
		6a-8c	$6_{(3)}$-$8_{(3)}$
		8a-6d	$8_{(3)}$-$6_{(1)}$
		10a-4e	$10_{(1)}$-$4_{(1)}$
		12a-2f	$12_{(1)}$-$2_{(1)}$
		14a	$14_{(3)}$
South Fork Eel	111SF4640	4a-6b-4e	$4_{(1)}$-$6_{(3)}$-$4_{(1)}$
		4a-10b	$4_{(1)}$-$10_{(1)}$
		6a-8c	$6_{(3)}$-$8_{(3)}$
		8a-6d	$8_{(3)}$-$6_{(1)}$
		10a-4e	$10_{(1)}$-$4_{(1)}$
		12a-2f	$12_{(1)}$-$2_{(1)}$
		14a	$14_{(3)}$

*Deployment day is the large number followed by the number of replicates in parenthetical subscript. For example, $4_{(1)}$ means a sampler was deployed for four days and not replicated, and $6_{(3)}$ means a sampler was deployed for six days and triplicated.

2.4 Laboratory Analysis

2.4.1 Laboratories and Reporting

During the study, the Regional Water Board used ELISA and LCMS to determine the cyanotoxin concentrations in SPATT and water grab samples. These analytical techniques were chosen based on laboratory availability and, in some cases, to determine what cyanotoxin congeners are dominant. ELISA and LCMS methods do not measure complimentary sets of cyanotoxin congeners in the sample analysis matrix, and the analytical methods differ in the way they derive the concentration values. Therefore, direct comparison of cyanotoxin concentrations between laboratory ELISA and LCMS methods is not possible. However, for the purposes of this report, no distinction is made in the results between the two laboratory methods, nor are comparisons made between methods.

2.4.2 Enzyme-Linked Immunosorbent Assay (ELISA)

ELISA detects and quantifies cyanotoxins using reactive proteins or antibodies. ELISA passively binds the cyanotoxins and their congeners to a membrane, then separates the non-bound material. A colorimetric measurement is then taken with the amount of toxin bound to the membrane being proportional to a color change in each well. ELISA measures multiple cyanotoxin congeners within a class of cyanotoxins and cannot

differentiate among congeners of a molecular structure. As a result, ELISA data are the total concentration of multiple detectable cyanotoxin congeners that may be in the sample. In this special study, ELISA was used to measure combined microcystins and nodularins (MCY/NOD) since these classes are cross-reactive. For more information on ELISA test kits and cross-reactivity among cyanotoxin congeners, see NCRWQCB 2022. All ELISA laboratory analyses were performed at the University of California at Santa Cruz using Abraxis manufactured kits.

2.4.3 Liquid Chromatography with Mass Spectrometry (LCMS)

LCMS is a technique to identify and quantify molecules in a sample. The technique uses liquid chromatography to separate different molecules within a sample and then uses mass spectrometry to ionize these molecules and measure their mass. LCMS results provide information on the structure, identity, and quantity of each specific cyanotoxin congener when compared to a known standard. Presently, standards are only available for a few cyanotoxin congeners, and LCMS analysis has limited ability to quantify the concentration of cyanotoxins congeners that do not have a standard. In this special study, LCMS analysis was used to measure anatoxin-a (ATX) and nodularin-R (NOD). Other congeners within anatoxin and nodularin classes were not measured. Analyses were performed at the University of California at Santa Cruz.

2.5 Data Processing and Interpretation

Data for this special study are reported using various summary statistics (e.g., means, percentages, coefficient of variation). Data are presented using a series of bar graphs, boxplots, scatterplots, and tables. When replication was sufficient, non-parametric statistics were used to determine significant differences among deployment groups and resin types.

ELISA and LCMS method detection limits (MDLs) varied per target cyanotoxin and sample type (Table 5). Values below the MDL were recorded as zeros. Due to the prevalence of non-detect data, means rather than medians were used to describe central tendencies of replicated samplers since medians returned zero values.

Table 5. Method detection limit (MDL) for each laboratory method and target cyanotoxin.

Method	Cyanotoxin	SPATT MDL (ng/g)	Water Grab MDL (ug/L)
LCMS	Anatoxin-a	0.25	0.5
	Nodularin-R	0.25	0.25
ELISA	Microcystins/nodularins	12.5	0.15

2.6 Data Quality

Regional Water Board staff followed all appropriate SOPs to assure the generation of data of known and documented quality. The data reported in the Results section and in the Appendices are SWAMP compliant. This means the following:

a) Sample container, preservation, and holding time specifications of all measurement systems have been applied and were achieved as specified;
b) All the quality checks required by SWAMP were performed at the required frequency;
c) All measurement system batches/runs included their internal quality checks and diagnostic checks (e.g., electrode mV value) and had functioned within their performance/acceptance criteria; and
d) All SWAMP measurement quality objectives (MQOs) were met.

As in any data collection effort, some trip batches, laboratory batches, or individual results did not meet all the conditions stated above, and the comprehensive list of these occurrences is available from Regional Water Board staff. However, these data are considered usable if the flaw or omission was not considered detrimental, and they were flagged as “estimated”. Data verification and validation procedures followed the SWAMP Quality Management Plan (Puckett 2002), the SWAMP Quality Assurance Program Plan (SWAMP 2008; SWAMP 2017b), and the SWAMP Quality Assurance Project Plan for bioassessments (SCCWRP 2009).

3 Results

3.1 Results for 4-Day Experiment

3.1.1 Detection Rates

Anatoxin-a was detected in all SPATT samplers at all rivers and sites (100%) during the 4-day experiment (Table 6). Microcystins/nodularins were detected in 69.2% of the samplers at Site 113NA9990 and detected in 38.5-100% of samplers at the three South Fork Eel River Sites 111SF2423, 111SF4640, and 111SF6856. Nodularin-R was detected in all samplers at Sites 113NA9990 and 111SF 6856, and 50.0-84.6% of samplers at Sites 111SF2423 and 111SF4640.

Table 6. Detection rates in SPATT samplers across all deployment groups for the 4-day experiment in the Navarro and South Fork Eel Rivers, 2019. ATX, anatoxin-a; MCY/NOD, microcystins/nodularins; NOD, nodularin-R.

River	Site	Statistic	ATX	MCY/NOD	NOD
Navarro	113NA9990	Detections	13	9	13
		Total Samples	13	13	13
		Detection Rate	100%	69.2%	100%
South Fork Eel River	111SF2423	Detections	12	6	6
		Total Samples	12	12	12
		Detection Rate	100%	50.0%	50.0%
	111SF4640	Detections	13	5	11
		Total Samples	13	13	13
		Detection Rate	100%	38.5%	84.6%
	111SF6856	Detections	6	8	8
		Total Samples	6	8	8
		Detection Rate	100%	100%	100%

SPATT samplers that were non-detect for cyanotoxins were further evaluated to determine whether the result was consistent with any replicates or concurrent samplers. Inconsistent non-detects are defined as cases when a SPATT sampler did not detect cyanotoxins while a replicate and/or concurrent sampler did detect cyanotoxins. The rate of inconsistent non-detects was calculated across all sites for each deployment group and cyanotoxin using the number of inconsistent non-detects per total samples. Across all deployment groups, no inconsistent non-detects were identified for samplers measuring anatoxin-a (Table 7). Inconsistent non-detects for samplers measuring microcystins/nodularins occurred in all deployment groups with rates ranging from 10.0-50.0%; the highest rate of inconsistent non-detects occurred in the three-day deployments with replicates detecting as high as 50.0 ng/g microcystins/nodularins. Rates of inconsistent non-detects for nodularin-R measurements ranged from 0.0-50.0% with the highest rate occurring during the three-day deployment.

Table 7. Rates of inconsistent non-detects in SPATT samplers across all sites for each deployment group and cyanotoxin during the 4-day experiment in the Navarro and South Fork Eel Rivers, 2019. Rates were calculated using the number of inconsistent non-detects per total samples. ATX, anatoxin-a; MCY/NOD, microcystins/nodularins; NOD, nodularin-R.

Deployment Group	Statistic	ATX	MCY/NOD	NOD
1a, 1b, 1c, 1d	Inconsistent Non-detects	0	9	0
	Total Samples	17	19	19
	Rate of Inconsistent Non-detects	0.0%	47.4%	0.0%
2a, 2c	Inconsistent Non-detects	0	5	1
	Total Samples	13	13	13
	Rate of Inconsistent Non-detects	0.0%	38.5%	7.7%
3a	Inconsistent Non-detects	0	2	2
	Total Samples	4	4	4
	Rate of Inconsistent Non-detects	0.0%	50.0%	50.0%
4a	Inconsistent Non-detects	0	1	0
	Total Samples	10	10	10
	Rate of Inconsistent Non-detects	0.0%	10.0%	0.0%

3.1.2 Comparing Deployment Groups

To determine the effects of deployment length on SPATT measurements, all one-day through four-day deployment groups were compared for each site and cyanotoxin. The mean concentration was used for replicated samplers that were deployed and retrieved on the same day. Anatoxin-a concentrations were variable, however, all deployment groups were within the same order of magnitude (Site 113NA990 range 15.5-63.8 ng/g; Site 111SF4640 range 214.2-747.0 ng/g; Site 111SF6856 range 4.2-8.6 ng/g) except for Site 111SF2423 (range 5.4-15.0 ng/g) (Figure 5). Anatoxin-a measurements from samplers 1a and 1b were not available at Site 111SF6856.

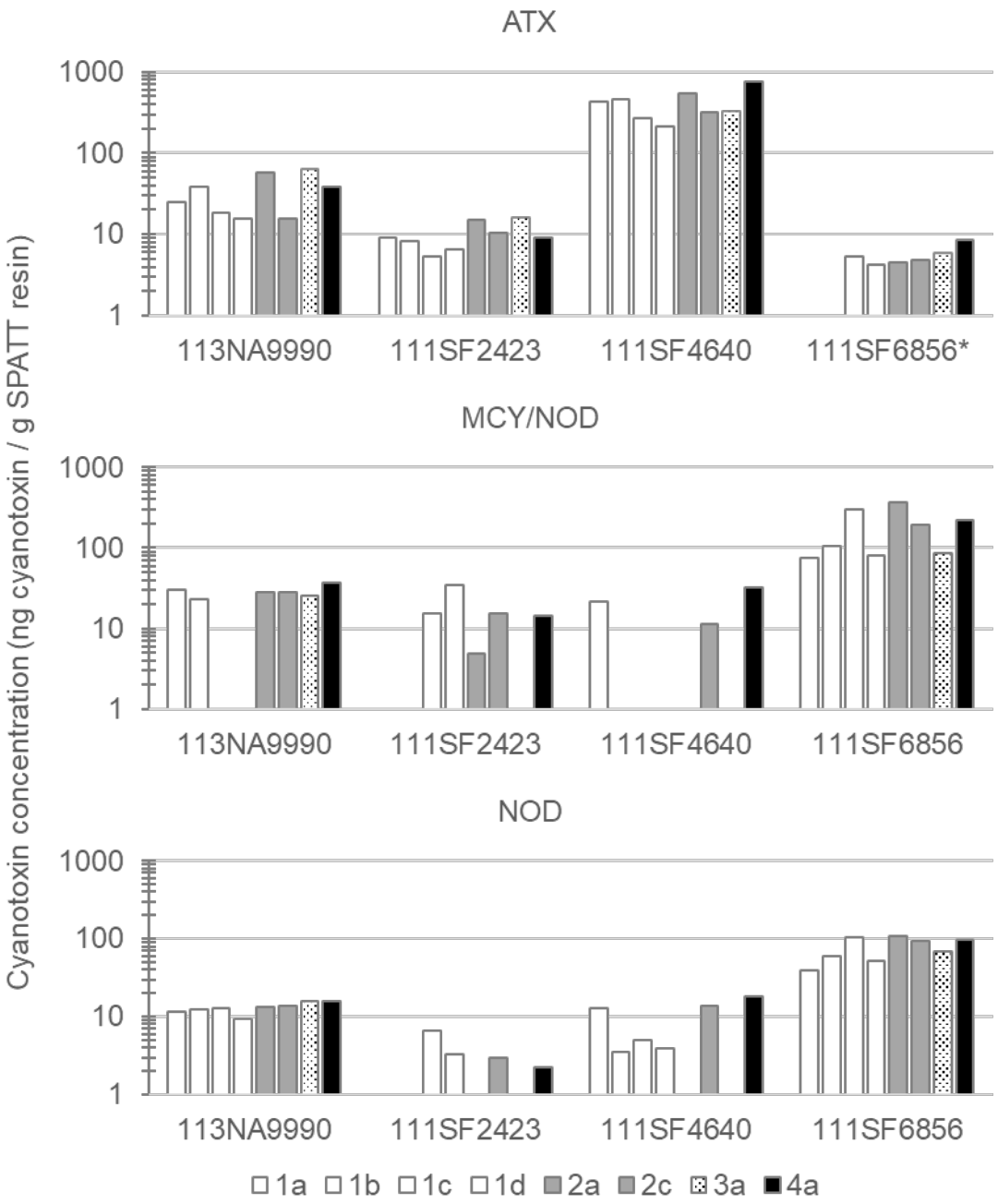

*Figure 5. Anatoxin-a (ATX), microcystins/nodularins (MCY/NOD), and nodularin-R (NOD) concentrations in SPATT samplers deployed during the 4-day experiment in the Navarro River and South Fork Eel River, 2019. *1a and 1b samplers are not available for Site 111SF6856.*

Microcystins/nodularins also varied within each site and across all deployment groups (Site 113NA9990 range ND-37.4 ng/g; Site 111SF2423 range ND-34.4 ng/g; Site 111SF4640 range ND-32.1 ng/g; Site 111SF6856 range 75.3-372.6 ng/g) (Figure 5). In contrast to anatoxin-a, microcystins/nodularins were not detected in single-day, two-

day, and three-day samplers at Sites 113NA9990, 111SF2423, and 111SF4640, but were detected in all samplers at Site 111SF6856.

Nodularin-R was detected in more single-day samplers than microcystins/nodularins at Sites 113NA9990 and 111SF4640, and less in two-day samplers at Site 111SF2423 (Figure 5). Aside from differences in non-detects, nodularin-R exhibited a similar pattern to microcystins/nodularins but at lower concentrations within each site (Site 113NA9990 range 9.4-15.9 ng/g; Site 111SF2423 range ND-6.6 ng/g; Site 111SF4640 range ND-17.9 ng/g; Site 111SF6856 range 39.1-109.1 ng/g).

A Kruskal-Wallis one-way analysis of variance or Mann-Whitney U-Test was used for each cyanotoxin within each site to determine significant differences ($\alpha = 0.05$) among deployment groups with three or two replicates, respectively. No samplers were replicated at Site 111SF6856, so this site was not included in the following analyses. There were no significant differences among deployment groups ($p > 0.05$) (Table 8).

*Table 8. Kruskal-Wallis or Mann-Whitney U-Test results to determine significant differences among deployment groups for replicated SPATT samplers within each site and cyanotoxin class during the 4-day experiment in the Navarro and South Fork Eel Rivers, 2019. *Mann-Whitney U-Test was used since only two replicates were available.*

Site	ATX		MCY/NOD		NOD	
	Test statistic	p-value	Test statistic	p-value	Test statistic	p-value
113NA9990	5.14	0.077	3.03	0.219	2.78	0.249
111SF2423*	1.65	0.100	-0.93	0.354	-1.86	0.064
111SF4640	7.53	0.570	3.75	0.290	5.44	0.142

A post-hoc Dunn's Test was used to determine which deployment groups differed significantly within each cyanotoxin class and site. A Bonferroni correction ($\alpha = 0.05$ / number of tests or pairs) was used to adjust significant levels to reduce the likelihood of Type 1 errors or false positives. At Site 113NA9990, anatoxin-a concentrations were significantly higher in the 4a deployments than the 2d deployments ($Z = 2.17$, $p = 0.030$) (Figure 6). At Site 111SF4640, anatoxin-a was significantly higher in the 4a deployments than the 1c deployments ($Z = 2.60$, $p = 0.009$). Post-hoc tests for Site 111SF2423 were not possible since only two replicates were available.

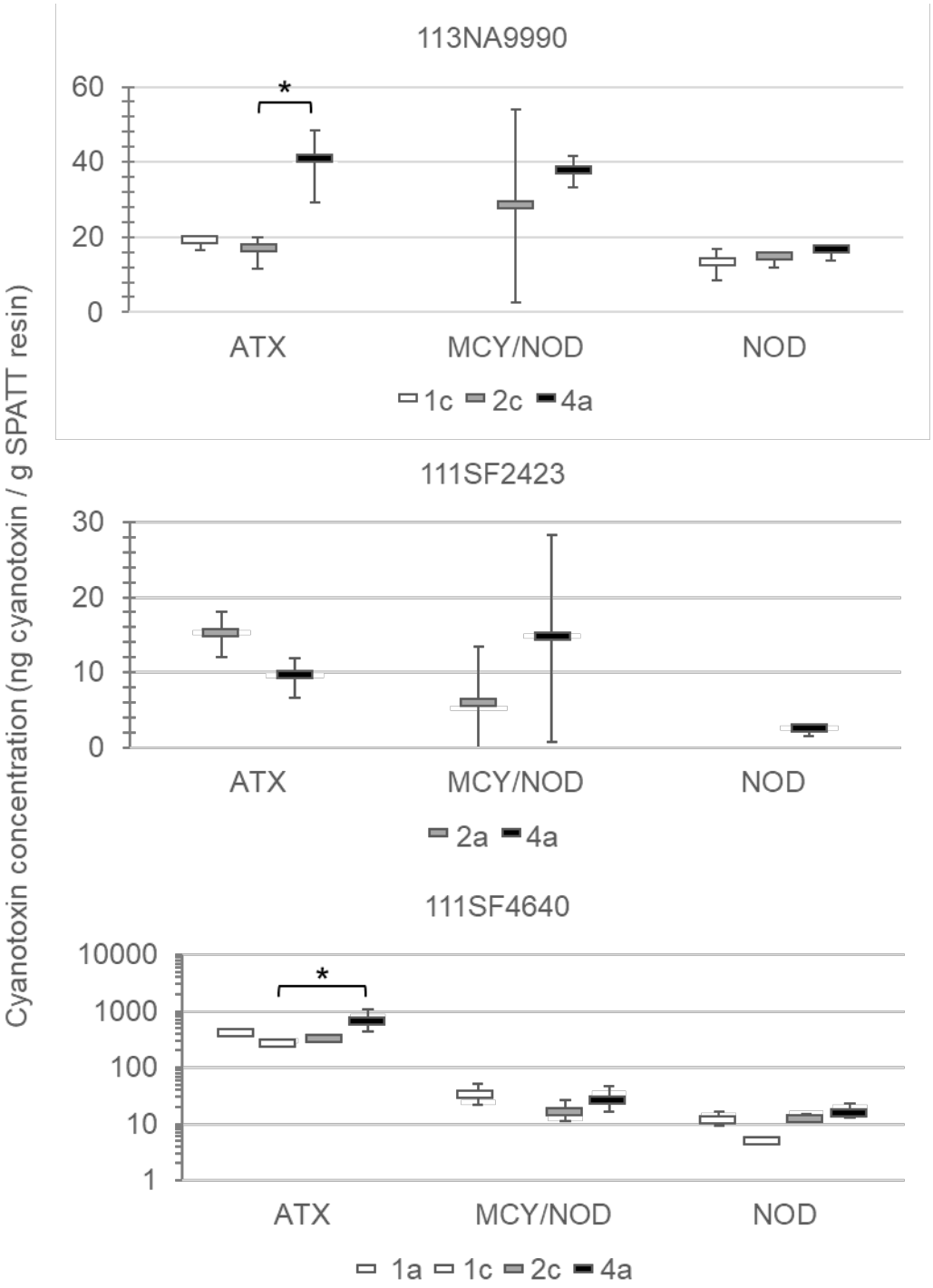

Figure 6. Mean and standard deviation of anatoxin-a (ATX), microcystins/nodularins (MCY), and nodularin-R (NOD) concentrations in replicated SPATT samplers during the 4-day experiment in the Navarro and South Fork Eel Rivers, 2019. Brackets and asterisk (*) indicate significant differences.

3.1.3 Cyanotoxin Concentrations Over Time

Concurrent deployments (i.e., 1a, 2a, 3a, 4a) were evaluated with linear regression models to determine whether the length of deployment affected concentrations of anatoxin-a, microcystins/nodularins, and nodularin-R at each site. Only the 1a, 2a, 3a, and 4a concurrent deployments were plotted since these all share a portion of deployment length and therefore experienced the same river conditions. Average values were used for deployments with replicate SPATTs. Most relationships were not significant and had a large amount of variance around the regression (Figure 7).

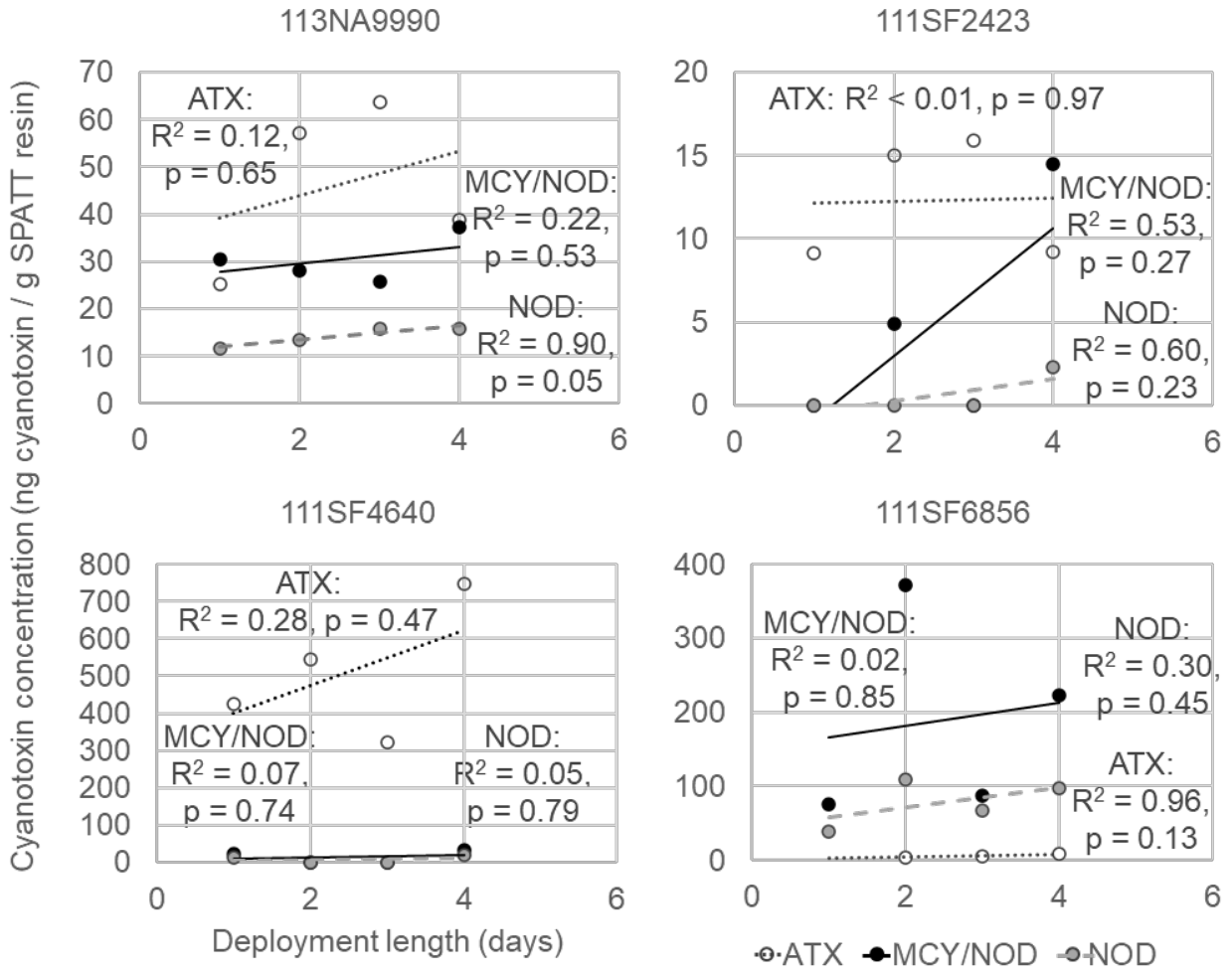

Figure 7. Correlations between deployment length and concentrations of anatoxin-a (ATX), microcystins/nodularins (MCY/NOD), and nodularin-R (NOD) for concurrent SPATT samplers (1a, 2a, 3a, and 4a) during the 4-day experiment in the Navarro and South Fork Eel Rivers, 2019.

At Site 113NA9990, fitted lines among cyanotoxins showed a comparable increase of cyanotoxin concentrations with increasing deployment length, although each cyanotoxin differed in concentrations. The regression model for nodularin-R explained the most

variance (R^2 = 0.8951) but was not statistically significant (p = 0.054) (Figure 7). At Site 111SF2423, correlations of anatoxin-a and nodularin-R showed slight increases with increasing deployment lengths while microcystins/nodularins exhibited a larger increase for the two detections on days 2 and 4; regression models differed in their ability to explain variance (R^2 range <0.01-0.60), and none were significant. At Site 111SF4640, the regression model for anatoxin-a explained the most variance, though it was very low (R^2 = 0.28) and exhibited a larger increase in concentrations with increasing deployment length than the regressions for microcystins/nodularins and nodularin-R, none of which were significant. At Site 111SF6856, all correlations showed an increase in cyanotoxin concentrations with increasing deployment length. The regression model for anatoxin-a explained the most variance (R^2 = 0.96) but was not significant.

3.1.4 Exploring Daily Variability of Cyanotoxins

To evaluate the influence of daily variability on cyanotoxin concentrations during longer deployments, consecutive single-day SPATT deployments (i.e., 1a, 1b, 1c, 1d) were compared to the concentrations for concurrent deployments (i.e., 1a, 2a, 3a, 4a). In Figures 8-10, consecutive single-day concentrations are depicted as bar graphs and concurrent deployments are plotted as a dotted line to illustrate changes in concentration over time.

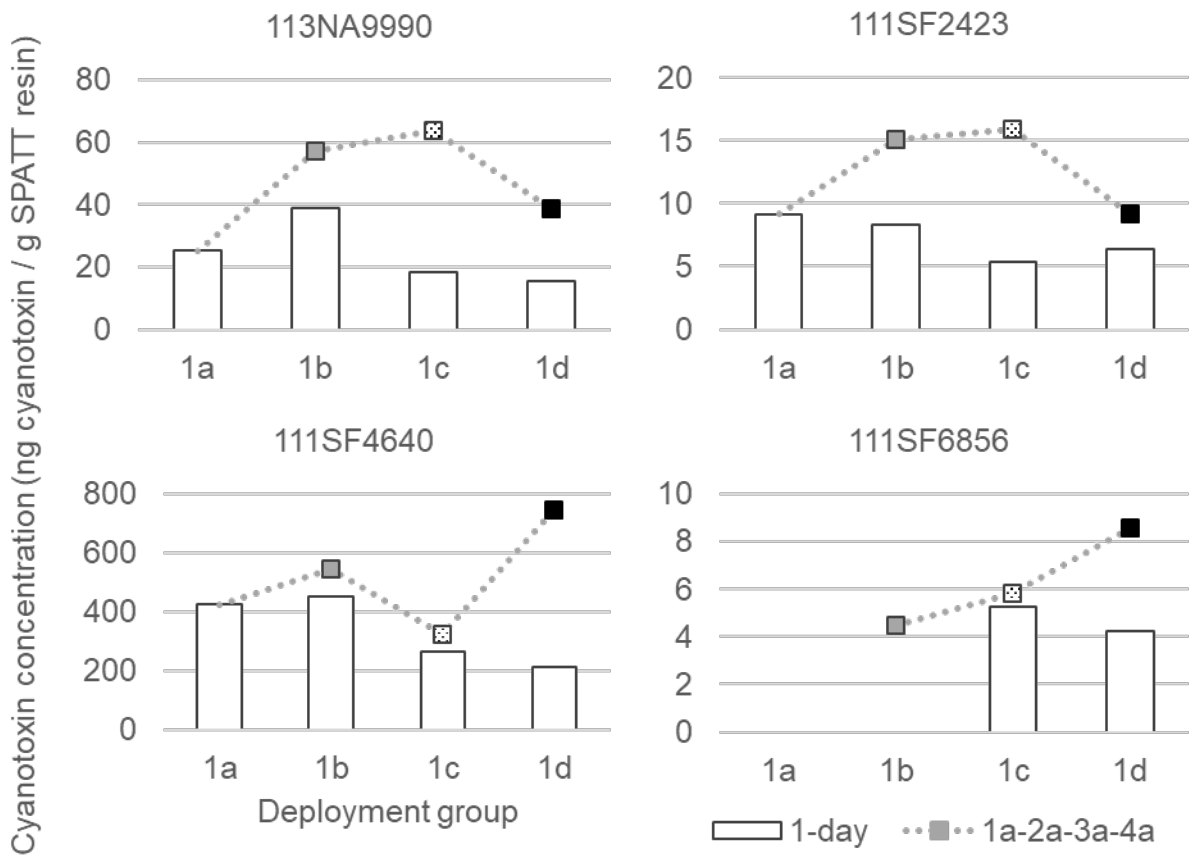

*Figure 8. Anatoxin-a (ATX) concentrations for single-day SPATT samplers (bars; 1a, 1b, 1c, 1d) and concurrent samplers (dotted line; 2a, 3a, 4a) for each site in the Navarro and South Fork Eel Rivers during the 4-day experiment, 2019. *1a and 1b samplers are not available for Site 111SF6856.*

Across all sites, anatoxin-a concentrations in concurrent deployments were higher than those in the single-day deployments (Figure 8). In some instances, single-day fluctuations were observable in the concurrent deployments. For example, at Site 113NA9990, a single-day increase on day 2 was observed in the concurrent 2a and 3a deployments then a decrease in the single-day deployments on days 3 and 4 were observed in the full-length deployment (4a).

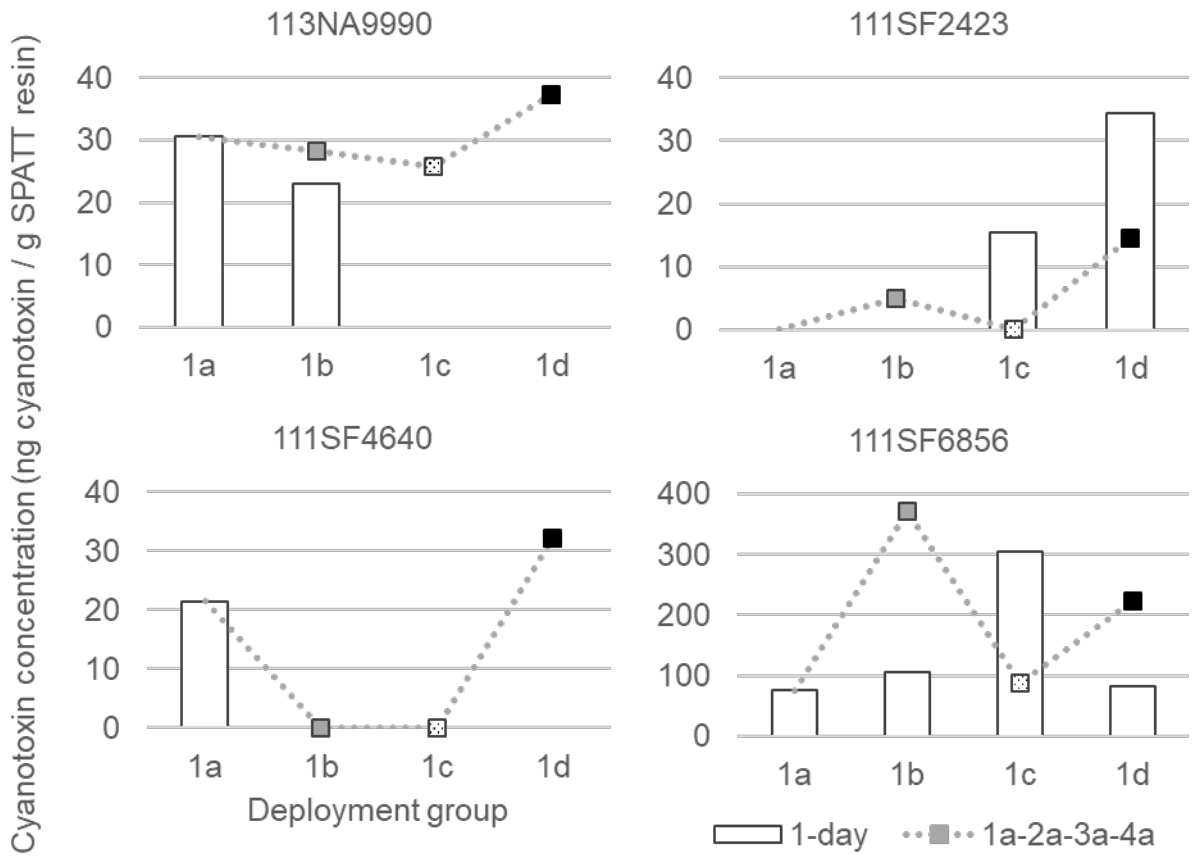

Figure 9. Microcystins/nodularins (MCY/NOD) concentrations for single-day SPATT samplers (bars; 1a, 1b, 1c, 1d) and concurrent samplers (dotted line; 1a, 2a, 3a, 4a) for each site in the Navarro and South Fork Eel Rivers during the 4-day experiment, 2019.

Single-day variability was not observable in concurrent deployments for microcystins/nodularins, and patterns were difficult to interpret due to several non-detect samplers (Figure 9). Depending on the site, microcystins/nodularins were higher in single-day (e.g., Site 111SF2423, days 3 and 4) or concurrent deployments (e.g., Site 111SF6856, days 2 and 4). Microcystins/nodularins were not detected in both single-day (e.g., Site 113NA9990, days 2 and 3) or concurrent samplers (e.g., Site 111SF4640, days 2 and 3).

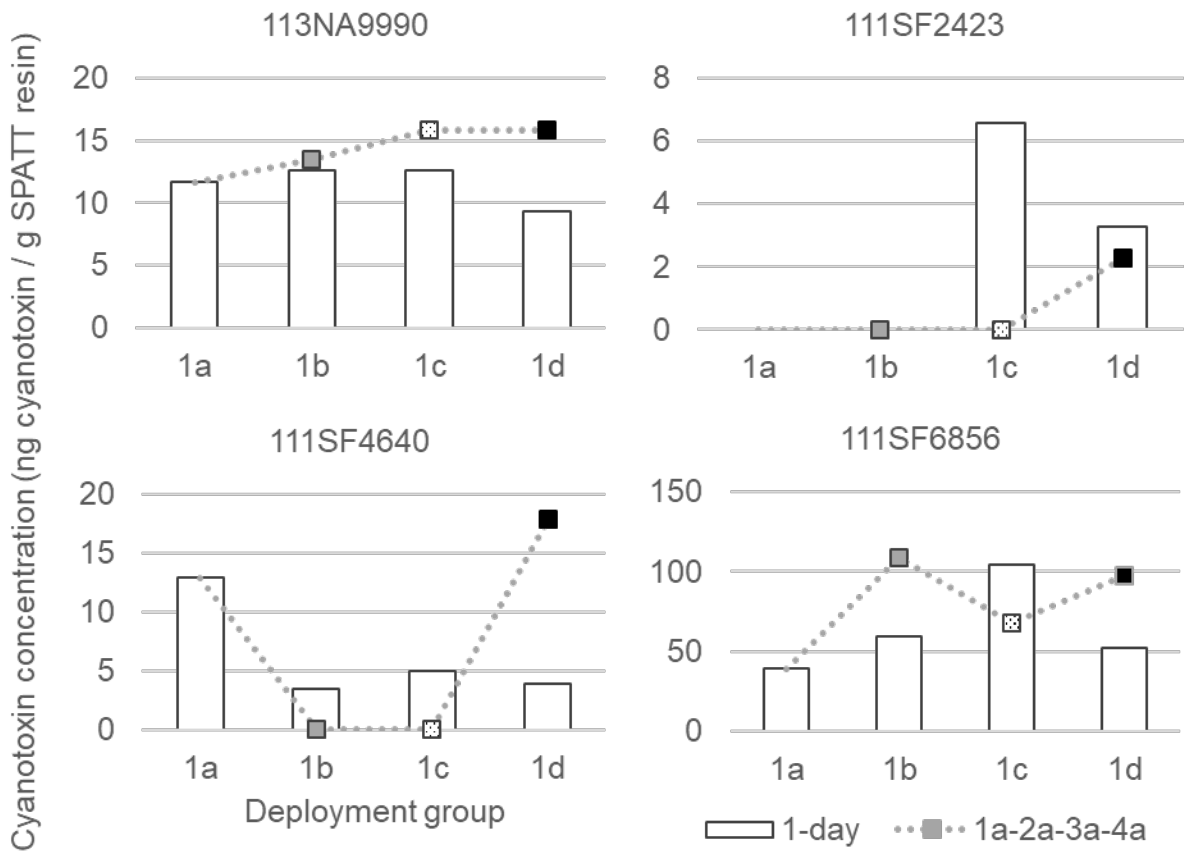

Figure 10. Nodularin-R (NOD) concentrations for single-day SPATT samplers (bars; 1a, 1b, 1c, 1d) and concurrent samplers (dotted line; 1a, 2a, 3a, 4a) for each site in the Navarro and South Fork Eel Rivers during the 4-day experiment, 2019.

The comparison of nodularin-R concentrations in single-day and concurrent deployments varied per site (Figure 10). At Site 113NA9990, nodularin-R concentrations were higher in concurrent deployments and appeared to follow the pattern in single-day deployments. For the other three sites, nodularin-R was higher in single-day (e.g., 111SF4640, day 4) or concurrent deployments (e.g., 111SF6856, day 3). Nodularin-R was not detected in both single-day (e.g., Site 111SF2423, days 1 and 2) or concurrent samplers (e.g., Site 111SF4640, days 2 and 3). Again, concentrations and patterns of nodularin-R were similar to microcystins/nodularins, however, each differed in the number of non-detects.

3.1.5 Comparing SPATT and Water Samples

Discrete ambient water column grab samples were collected at the start of the 4-day experiment (i.e., day 0) and for each consecutive day to determine if any detections corresponded with single-day SPATT measurements. At Site 113NA9990, anatoxin-a was not detected in water grab samples except for the 0.14 ug/L measurement on the second day (Table 9) while SPATTs at this site had a 100% detection rate (Table 6). The single water grab detection corresponds to increased anatoxin-a concentrations

measured in sampler 1b, the second single-day SPATT deployment at Site 113NA9990 (Figure 8). Microcystins/nodularins were not detected in water grab samples except for the 0.28 ug/L measurement at the start of the experiment at Site 111SF2423; however, the first single-day SPATT deployment (1a) at this site did not capture this increased ambient concentration (Figure 9). SPATTs at Site 111SF2423 had a 50% detection rate for microcystins/nodularins. Nodularin-R was not detected in any water grab samples across all sites while SPATTs detections ranged from 50-100% (Table 6).

Table 9. Anatoxin-a (ATX), microcystins/nodularins (MCY/NOD), and nodularin-R (NOD) concentrations in ambient water column grab samples collected daily in the Navarro and South Fork Eel Rivers during the 4-day experiment, 2019. Samples with detections are bolded. "---" indicates no sample was collected.

Site	Day	ATX (ug/L)	MCY/NOD (ug/L)	NOD (ug/L)
113NA9990	0	ND	ND	ND
	1	ND	ND	ND
	2	**0.14**	ND	ND
	3	ND	ND	ND
	4	ND	ND	ND
111SF2423	0	ND	**0.28**	ND
	1	---	---	---
	2	ND	ND	ND
	3	ND	ND	ND
	4	---	---	---
111SF4640	0	---	---	---
	1	ND	ND	ND
	2	ND	ND	ND
	3	ND	ND	ND
	4	ND	ND	ND
111SF6856	0	ND	ND	ND
	1	ND	ND	ND
	2	ND	ND	ND
	3	ND	ND	ND
	4	ND	ND	ND

3.1.6 Evaluating Integrative Performance

To determine whether adsorption rates are additive or integrative during the 4-day experiment, SPATT cumulative measurements of anatoxin-a, microcystins/nodularins, and nodularin-R for multiple single-day and/or shorter concurrent deployments were compared to their corresponding full-length deployment. For instance, cumulative measurements for 1a+1b were compared to 2a, cumulative measurements for 1a+1b+1c as well as 2a+1c were compared to 3a, and cumulative measurements for

3a+1d as well as 2a+2c were compared to 4a. Averages were used for deployment groups with replicate SPATTs. Additive concentrations of shorter deployments were expressed as a percentage of their corresponding full-length deployment, which is represented by the dashed line below (Figure 11). Overall, summing cyanotoxin concentrations for the shorter concurrent deployments generally exceeded the concentrations of samplers deployed for the entire time period. Cumulative non-detects are represented by missing bars below.

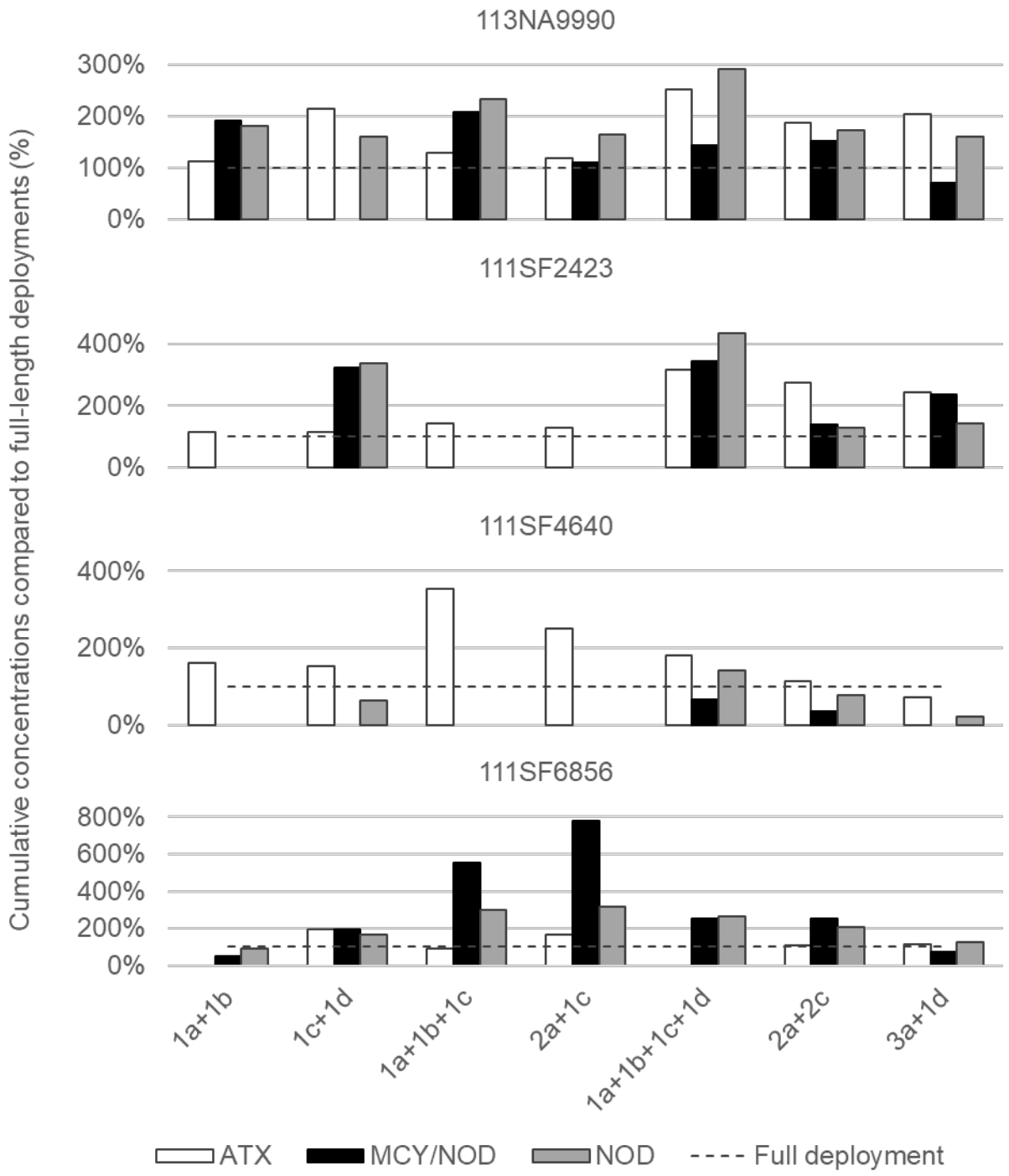

Figure 11. The percentage of anatoxin-a (ATX), microcystins/nodularins (MCY/NOD), and nodularin-R (NOD) concentrations in single-day and/or shorter concurrently deployed SPATT samplers compared to corresponding full-length deployments for each site in the Navarro and South Fork Eel Rivers during the 4-day experiment, 2019.

To summarize the data in Figure 11 above, additive concentrations across all cyanotoxin results were counted as lower than their full-length sampler (<75%), within

range of their full-length sampler (75-125%), or higher than their full-length sampler (>125%) for each site (Table 10). The sum of single-day and/or shorter concurrently deployed SPATT samplers tended to be higher than their corresponding full-length sampler except for Site 111SF4640, which was lower due to several non-detects for microcystins/nodularins and nodularin-R. During most deployments, the full-length sampler under-integrated the amount of cyanotoxins in the water.

Table 10. Number of additive deployment lengths that are lower (<75%), within range (75-125%), or higher (>125%) than their corresponding full-length sampler for each site during the 4-day experiment in the Navarro and South Fork Eel Rivers, 2019.

Site	Number of Additive Deployments								
	<75% of full-length			75-125% of full-length			>125% of full-length		
	ATX	MCY	NOD	ATX	MCY	NOD	ATX	MCY	NOD
113NA9990	0	2	0	2	1	0	5	4	7
111SF2423	0	3	3	2	0	0	5	4	4
111SF4640	1	7	5	1	0	1	5	0	1
111SF6856	2	1	0	3	1	2	2	5	5
Total:	3	13	8	8	2	3	17	13	17
	24			13			47		

3.1.7 Calculating Sampler Variability

To evaluate variation and repeatability in results during the 4-day experiment, replicate SPATT samplers were deployed on nine occasions across three sites (Table 11). Replicates were either duplicates or triplicates depending on the deployment group and site. The coefficient of variation was calculated for replicated samplers (CV = standard deviation / mean) to measure the level of dispersion around the mean, with a higher coefficient of variation meaning greater variability. Across all sites, cyanotoxin measurements among replicates had coefficients of variation ranging from 0.03-0.41 for anatoxin-a, 0.11-1.73 for microcystins/nodularins, and 0.06-0.33 for nodularin-R. The average coefficient of variation was similar for anatoxin-a (0.18) and nodularin-R (0.21), but higher for microcystins/nodularins (1.00).

Table 11. Anatoxin-a (ATX), microcystins/nodularins (MCY/NOD), and nodularin-R (NOD) concentrations for replicated SPATT samplers in the Navarro and South Fork Eel Rivers during the 4-day experiment, 2019. Summary statistics include number of samples (N), mean values, standard deviation (SD), coefficient of variation (CV), and non-detect (ND).

River	Site	Deployment Schedule	N	ATX (ng/g)			MCY/NOD (ng/g)			NOD (ng/g)		
				Mean	SD	CV	Mean	SD	CV	Mean	SD	CV
Navarro	113NA9990	1c	2	18.3	1.8	0.09	ND	---	---	12.6	4.1	0.32
	113NA9990	2c	3	15.7	4.2	0.26	28.4	25.7	0.90	13.8	1.8	0.13
	113NA9990	4a	3	38.9	9.6	0.25	37.4	4.1	0.11	15.8	2.0	0.13
South Fork Eel	111SF2423	2a	3	15.0	3.0	0.20	4.9	8.5	1.73	ND	---	---
	111SF2423	4a	3	9.2	2.6	0.29	14.5	13.8	0.95	2.3	0.7	0.33
	111SF4640	1a	2	425	18.7	0.04	21.5	30.4	1.41	12.9	3.7	0.29
	111SF4640	1c	2	267	19.1	0.07	ND	---	---	5.0	0.6	0.12
	111SF4640	2c	2	314	8.9	0.03	11.1	15.7	1.41	14.0	0.8	0.06
	111SF4640	4a	3	747	308	0.41	32.1	15.5	0.48	17.9	4.9	0.27
					Mean CV:	0.18		**Mean CV:**	1.00		**Mean CV:**	0.21

3.2 Results for 14-Day Experiment

3.2.1 Detection Rates

Across both HLB and HP20 resin types, anatoxin-a detections in SPATT samplers ranged from 86.4-90.9% at Site 114RR5407 and 90.9-100% at Site 111SF4640 in the 14-day experiment (Table 12). Detection rates for microcystins/nodularins ranged from 63.6-72.7% and 68.2-95.5% at Sites 114RR5407 and 111SF4640, respectively. Nodularin-R was detected in 95.5-100.0% of the samplers at Site 114RR5407, however, there were no detections at Site 111SF4640 for both resin types. Across all sites and cyanotoxins, HP20 had higher detection rates with the exception of anatoxin-a at Site 111SF4640.

Table 12. Detection rates for SPATT samplers across all deployment groups for both resin types in the 14-day experiment in the Russian and South Fork Eel Rivers, 2019. ATX, anatoxin-a; MCY/NOD, microcystins/nodularins; NOD, nodularin-R.

Site	Resin	Statistic	ATX	MCY/NOD	NOD
114RR5407	HLB	Detections	19	14	21
		Total Samples	22	22	22
		Detection Rate	86.4%	63.6%	95.5%
	HP20	Detections	20	16	22
		Total Samples	22	22	22
		Detection Rate	90.9%	72.7%	100%
111SF4640	HLB	Detections	22	15	0
		Total Samples	22	22	22
		Detection Rate	100%	68.2%	0.0%
	HP20	Detections	20	21	0
		Total Samples	22	22	22
		Detection Rate	90.9%	95.5%	0.0%

Similar to the 4-day experiment, SPATT samplers that were non-detect for a cyanotoxin were further evaluated to determine whether the result was consistent with any replicates or concurrent samplers. Inconsistent non-detects are defined as cases when a SPATT sampler did not detect cyanotoxins while a replicate and/or concurrent sampler did detect cyanotoxins. Rates of inconsistent non-detects were then calculated across all sites for each deployment length, cyanotoxin, and resin type. Rates of inconsistent non-detects were higher and more frequent across both resin types when measuring microcystins/nodularins (range 7.1-50.0%) with the highest rates occurring in the 10- and 12-day deployments (Table 13). Rates of inconsistent non-detects for anatoxin-a were only identified in three samplers across both resin types (4- and 6-day deployments; range 14.3-25.0%), while only one HLB sampler was identified as an inconsistent non-detect for nodularin-R (10-day deployment; 25.0%). Overall, HP20 samplers had lower rate of inconsistent non-detects except for the one sampler for

anatoxin-a during the 4-day deployments. For HP20 samplers, replicates of inconsistent non-detects measured as high as 83.2 ng/g for microcystins/nodularins while no replicates had inconsistent non-detects for anatoxin-a and nodularin-R. For HLB samplers, replicates with inconsistent non-detects measured as high as 321.7 ng/g for microcystins/nodularins but only 3.2 ng/g for anatoxin-a and no replicates with inconsistent non-detects for nodularin-R. Across all cyanotoxins and resin types, average rates of inconsistent non-detects were lowest for the 2-, 4-, and 8-day deployments.

Table 13. Rates of inconsistent non-detects in SPATT samplers across all sites for each deployment group, cyanotoxin, and resin type during the 14-day experiment in the Russian and South Fork Eel Rivers, 2019. Rates were calculated using the number of inconsistent non-detects per total samples. ATX, anatoxin-a; MCY/NOD, microcystins/nodularins; NOD, nodularin-R.

Deployment Group	Statistic	ATX		MCY/NOD		NOD	
		HLB	HP20	HLB	HP20	HLB	HP20
2f	Inconsistent Non-detects	0	0	0	0	0	0
	Total Samples	2	2	2	2	2	2
	Rate of Inconsistent Non-detects	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%
4a, 4e	Inconsistent Non-detects	0	1	0	0	0	0
	Total Samples	4	4	4	4	4	4
	Rate of Inconsistent Non-detects	0.0%	25.0%	0.0%	0.0%	0.0%	0.0%
6a, 6b, 6d	Inconsistent Non-detects	2	0	5	1	0	0
	Total Samples	14	14	14	14	14	14
	Rate of Inconsistent Non-detects	14.3%	0.0%	35.7%	7.1%	0.0%	0.0%
8a, 8c	Inconsistent Non-detects	0	0	2	0	0	0
	Total Samples	12	12	12	12	12	12
	Rate of Inconsistent Non-detects	0.0%	0.0%	16.7%	0.0%	0.0%	0.0%
10a, 10b	Inconsistent Non-detects	0	0	2	1	1	0
	Total Samples	4	4	4	4	4	4
	Rate of Inconsistent Non-detects	0.0%	0.0%	50.0%	25.0%	25.0%	0.0%
12a	Inconsistent non-detects	0	0	1	1	0	0
	Total Samples	2	2	2	2	2	2
	Rate of Inconsistent Non-detects	0.0%	0.0%	50.0%	50.0%	0.0%	0.0%
14a	Inconsistent Non-detects	0	0	2	0	0	0
	Total Samples	6	6	6	6	6	6
	Rate of Inconsistent Non-detects	0.0%	0.0%	33.3%	0.0%	0.0%	0.0%

3.2.2 Comparing Deployment Groups and Resins

To evaluate differences in deployment groups and resin types, measurements of anatoxin-a, microcystins/nodularins, and nodularin-R in HLB and HP20 samplers were compared for each deployment group at each site. The average concentration was used for deployment events with replicates. Cyanotoxin concentrations varied per resin type, deployment length, and river (Figures 12 and 13).

At Site 114RR5407, anatoxin-a in HLB samplers was not detected in one deployment (4a) and detectable concentrations ranged from 1.1 to 8.7 ng/g (Figure 12). HP20 samplers did not detect anatoxin-a in two deployments (4a, 4e) and detectable concentrations ranged from 2.1-17.3 ng/g with the highest concentration measured in the full-length (14a) deployment. Microcystins/nodularins in HLB samplers were not detected in three deployments (4a, 10a, 10b) and detections ranged from 25.1-192.4 ng/g with the highest concentration measured in the 12a deployment. Microcystins/nodularins in HP20 samplers were not detected in five deployments (2f, 4e, 6d, 10a, 12a) and detections ranged from 37.9-79.1 ng/g with concentrations peaking in the 8c deployment. Excluding one non-detection (10b) and a peak concentration in the 4e deployment in HLB samplers, nodularin-R concentrations in HLB samplers (range 13.3-80.3 ng/g) and HP20 samplers (range 24.8-53.7 ng/g) followed a similar pattern, though HLB concentrations tended to be higher.

At Site 111SF4640, anatoxin-a concentrations were higher in HLB samplers, which ranged from 3.9-9.5 ng/g with the highest concentrations occurring in the full-length deployment (14a) (Figure 13). In the HP20 samplers, anatoxin-a was not detected in two deployments (2f, 4e) and detections were lower (range 1.7-4.1 ng/g) with highest concentrations in the 10b deployment. Microcystins/nodularins in HLB samplers were not detected in three deployments (2f, 4e, 12a) and detections ranged from 18.5-141.3 ng/g with the highest concentrations in the 8c deployment. In the HP20 samplers, microcystins/nodularins were not detected in one deployment (2f) and detections ranged from ND-107.3 ng/g with the highest concentrations in the 6a deployment. Nodularin-R was not detected by either resin types in any samplers at Site 111SF4640 and therefore is not included in the figure below.

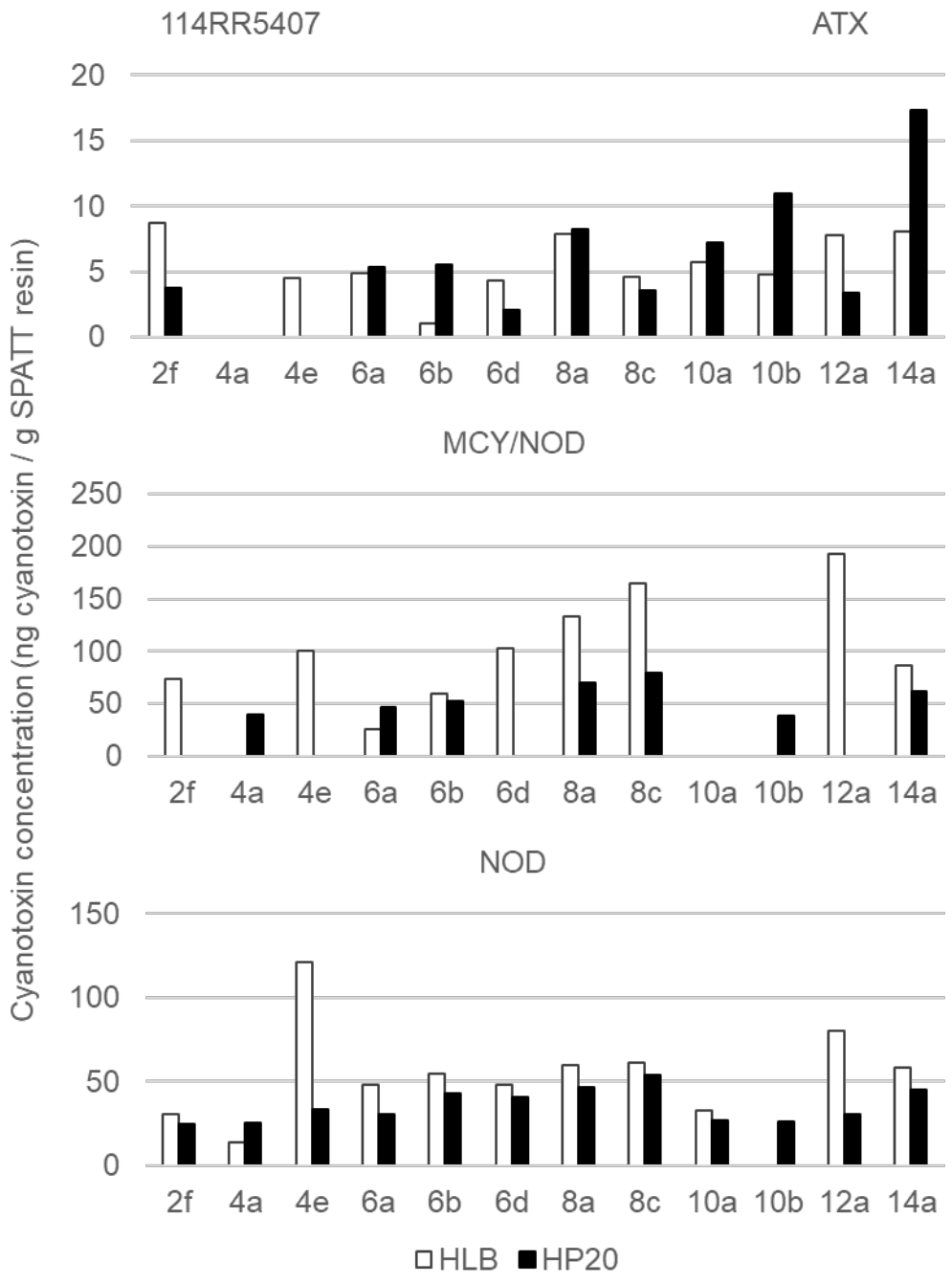

Figure 12. Anatoxin-a (ATX), microcystins/nodularins (MCY/NOD), and nodularin-R (NOD) concentrations in SPATT samplers constructed with HLB and HP20 resins at Site 114RR5407 during the 14-day experiment, 2019.

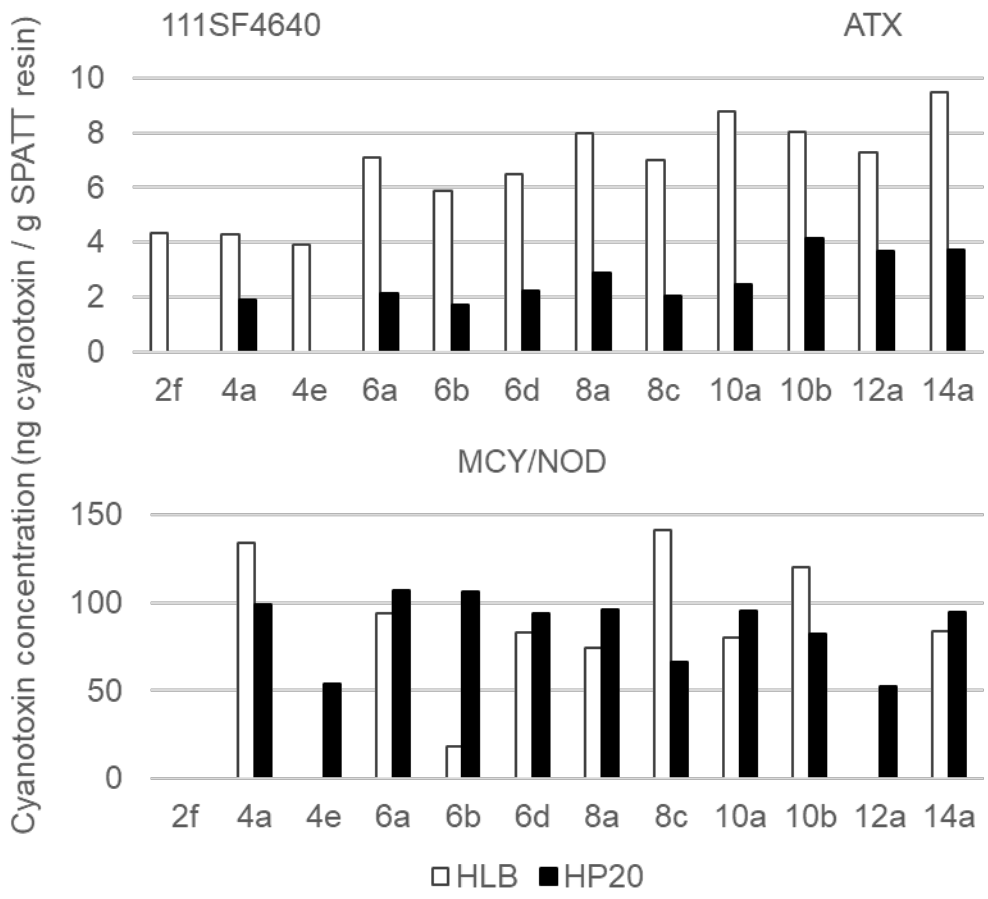

Figure 13. Anatoxin-a (ATX) and microcystins/nodularins (MCY/NOD) concentrations in SPATT samplers constructed with HLB and HP20 resins at Site 111SF4640 during the 14-day experiment, 2019. Nodularin-R (NOD) was not detected.

For replicated samplers, a Kruskal-Wallis one-way analysis of variance was used for each cyanotoxin within each site to determine significant differences ($\alpha = 0.05$) among deployment lengths. At Site 114RR5407, anatoxin-a concentrations were significantly different among deployment groups of HLB samplers ($H_4 = 10.85$, $p = 0.028$) and not significant for HP20 samplers ($H_4 = 9.17$, $p = 0.057$) (Table 14). Nodularin-R concentrations were also not significant among deployment groups of HP20 samplers ($H_4 = 8.37$, $p = 0.079$) at Site 114RR5407. All samplers at Site 111SF4640 were non-detect for nodularin-R and were not included in the analysis.

Table 14. Kruskal-Wallis results for replicated SPATT samplers within each site and cyanotoxin class during the 14-day experiment in the Russian and South Fork Eel Rivers, 2019. Significant values (p<0.05) are bolded.

Site	Resin	ATX		MCY/NOD		NOD	
		Test statistic	p-value	Test statistic	p-value	Test statistic	p-value
114RR5407	HLB	10.85	**0.028**	3.87	0.424	0.77	0.943
	HP20	9.17	0.057	4.40	0.355	8.37	0.079
111SF4640	HLB	4.67	0.323	6.30	0.178	---	---
	HP20	5.37	0.252	5.17	0.271	---	---

A post-hoc Dunn's Test was used to determine which deployment groups differed significantly within each cyanotoxin class and site. A Bonferroni correction (α = 0.05 / number of tests or pairs) was used to adjust significant levels to reduce the likelihood of Type 1 errors or false positives. At Site 114RR5407, anatoxin-a concentrations among HLB samplers were significantly higher in the 14a deployments than the 6b deployments (Z = 3.02, p = 0.003) (Figure 14). For HP20 samplers at Site 113RR5407, anatoxin-a was significantly higher in the 14a deployments than the 8c deployments (Z = 2.92, p = 0.003) and nodularin-R was significantly higher in the 8c deployments than the 6a deployments (Z = 2.83, p = 0.004). There were no significant differences among deployment groups of HLB or HP20 samplers at Site 111SF4640 (Figure 15).

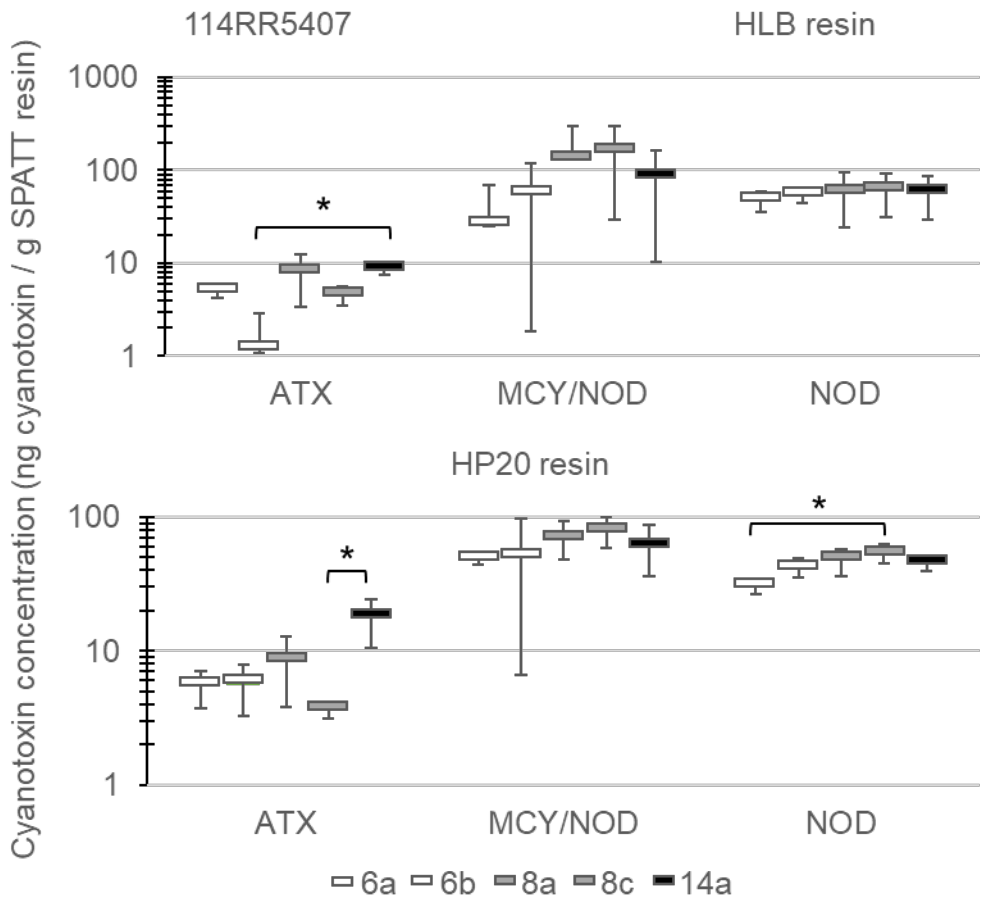

Figure 14. Mean and standard deviation of anatoxin-a (ATX), microcystins/nodularins (MCY), and nodularin-R (NOD) concentrations in replicated SPATTs for each deployment group within HLB and HP20 resin types at Site 114RR5407 during the 14-day experiment, 2019. Brackets and asterisks (*) indicate significant differences.

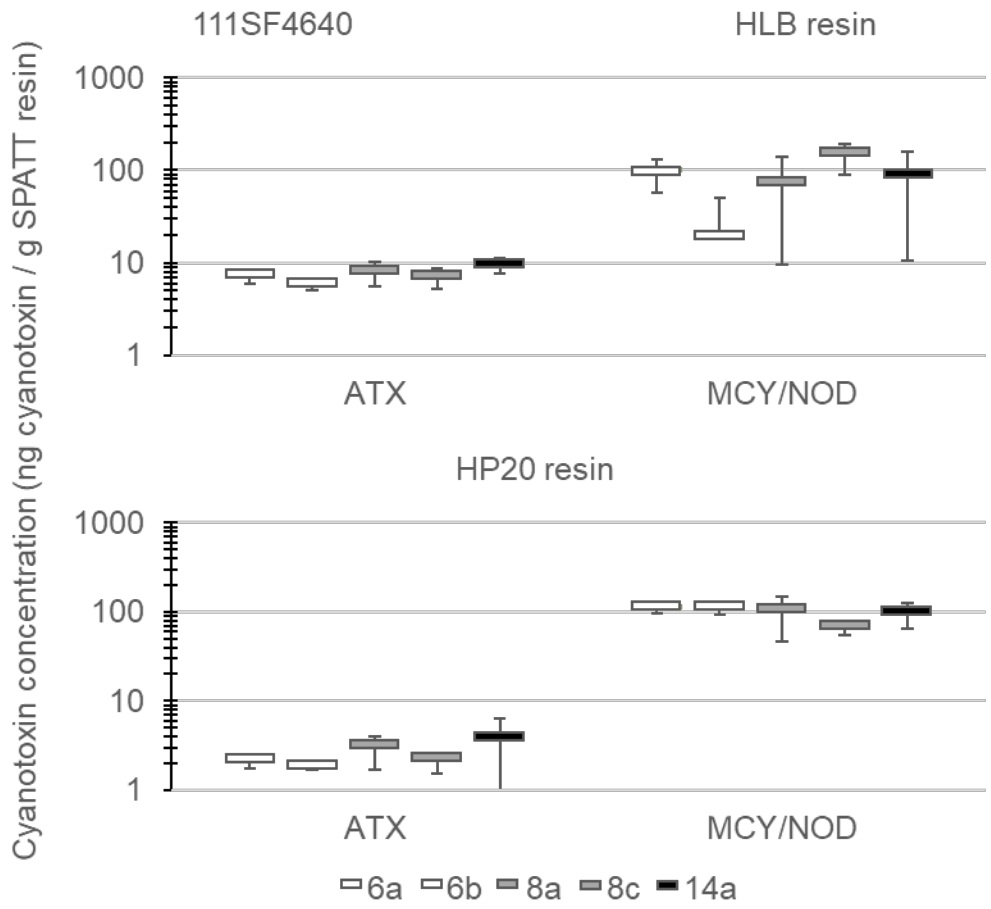

Figure 15. Mean and standard deviation of anatoxin-a (ATX) and microcystins/nodularins (MCY) concentrations in replicated SPATTs for each deployment group within HLB and HP20 resin types at Site 111SF4640 during the 14-day experiment, 2019. Brackets and asterisks (*) indicate significant differences.

Since all deployments consisted of paired HLB and HP20 samplers, a paired Wilcoxon Signed-Rank test was used across all SPATTs to determine which resin type adsorbed significantly higher concentrations of each cyanotoxin class at each site (Table 15). At Site 114RR5407, concentrations were significantly higher in HLB samplers than HP20 samplers for nodularin-R ($t_{21} = 2.35$, $p = 0.018$). At Site 111SF4640, anatoxin-a concentrations were significantly higher in HLB samplers than HP20 samplers ($t_{21} = 4.77$, $p < 0.001$). All samplers at Site 111SF4640 were non-detect for nodularin-R and were not included in the analysis.

Table 15. Paired Wilcoxon Signed-Rank test results for all SPATT samplers within each site and cyanotoxin class during the 14-day experiment in the Russian and South Fork Eel Rivers, 2019. Significant values (p<0.05) are bolded.

Site	ATX		MCY/NOD		NOD	
	Test statistic	p-value	Test statistic	p-value	Test statistic	p-value
114RR5407	-1.10	0.272	1.58	0.114	2.35	**0.018**
111SF4640	4.77	**< 0.001**	-0.683	0.495	---	---

3.2.3 Cyanotoxin Concentrations Over Time

Concurrent deployments were evaluated with linear regression models to analyze whether the length of deployment affected concentrations of anatoxin-a, microcystins/nodularins, and nodularin-R in SPATT samplers constructed with either HLB or HP20 resin. Two sets of concurrent deployments were plotted for each site: 1) 4a, 6a, 8a, 10a, 12a; and 2) 2f, 4e, 6d, 8c, 10b, 14a. Each set of concurrent deployments share a portion of deployment length and therefore experienced the same river conditions: the first set of concurrent samplers were deployed at the start of the experiment while the second set of concurrent samplers were deployed on successive days (Figure 4). To illustrate changes over time, both sets of concurrent deployments are plotted with increasing time on the x-axis. Average values were used for deployments that were replicated.

At Site 114RR5407, anatoxin-a concentrations in the first set of concurrent deployments exhibited a similar positive response for both resin types, however, the HP20 regression model was more variable (R^2 = 0.5257, p = 0.103) than HLB (R^2 = 0.6553, p = 0.051) and both regressions were not significant (Figure 16). In the second set of concurrent deployments, the regression models for HP20 samplers were also positive and explained significantly more variability in anatoxin-a concentrations over time (R^2 = 0.7696, p = 0.022) while there was no discernible relationship in HLB samplers (R^2 = 0.0038, p = 0.908).

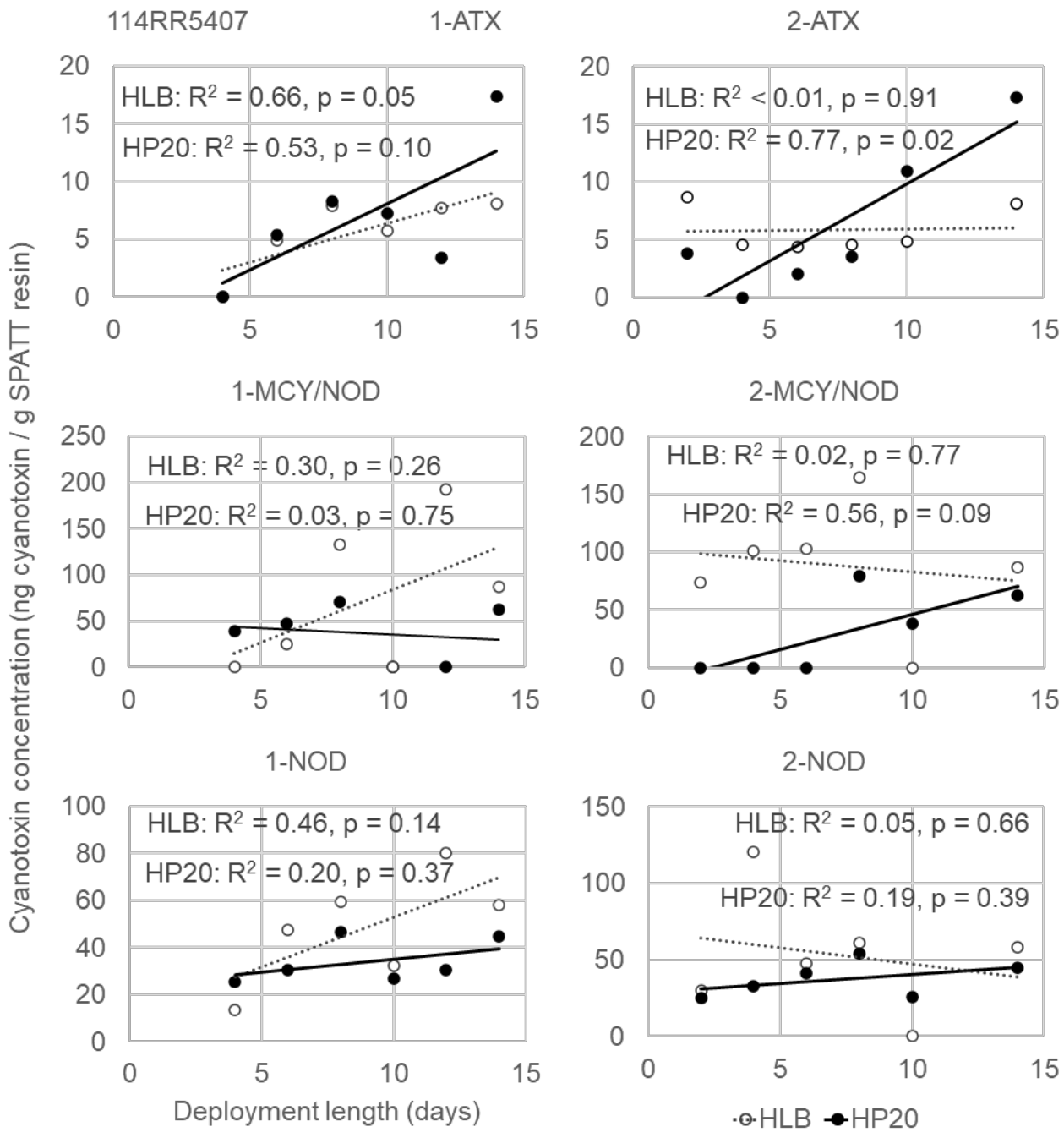

Figure 16. Correlations between deployment length and concentrations of anatoxin-a (ATX), microcystins/nodularins (MCY/NOD), and nodularin-R (NOD) in SPATT samplers constructed with HLB and HP20 resins at Site 114RR5407 during the 14-day experiment, 2019. The left and right panels compare the (1) 4a, 6a, 8a, 10a, 12a and (2) 2f, 4e, 6d, 8c, 10b, 14a concurrently deployed samplers, respectively.

Microcystins/nodularins at Site 114RR5407 either increased or decreased with increasing deployment length depending on the resin type and set of concurrent

deployments, however, no regression models were significant (Figure 16). With the exception of the positive regression model for HP20 samplers in the first set of concurrent deployments, nodularin-R exhibited a similar pattern to those of microcystins/nodularins, although at lower concentrations (Figure 16). None of the correlations between nodularin-R and deployment length were significant.

At Site 111SF4640, anatoxin-a concentrations across both sets of concurrent deployments and resin type exhibited a similar positive response with deployment length (Figure 17). All anatoxin-a regression models were significant ($p < 0.05$) at Site 111SF4640 with concentrations being higher in HLB samplers.

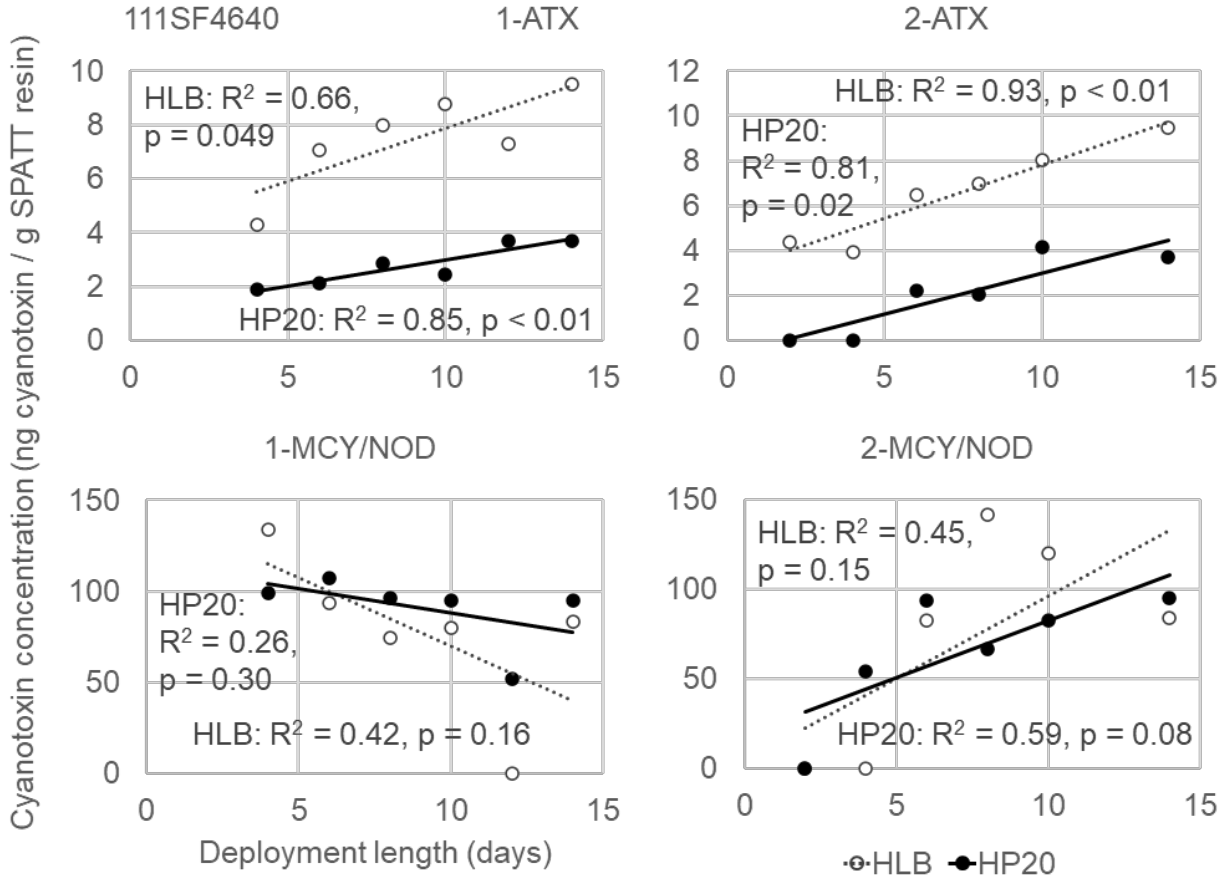

Figure 17. Correlations between deployment length and concentrations of anatoxin-a (ATX), microcystins/nodularins (MCY/NOD), and nodularin-R (NOD) in SPATT samplers constructed with HLB and HP20 resins at Site 111SF4640 during the 14-day experiment, 2019. The left and right panels compare the (1) 4a, 6a, 8a, 10a, 12a and (2) 2f, 4e, 6d, 8c, 10b, 14a concurrently deployed samplers, respectively.

For both resin types at Site 111SF4640, microcystins/nodularins concentrations had a negative relationship over time in the first set of concurrent deployments and a positive relationship in the second set of concurrent deployment lengths (Figure 17). These

regression models varied in their ability to explain variance (R^2 range 0.26-0.59) and none were significant. Due to the contrasting deployment schedules for each set of concurrent samplers, the negative response in the first set of samplers (1-MCY/NOD) and positive response in the second set (2-MCY/NOD) is expected if water column concentrations were decreasing over the course of the study, which would result in lower concentrations in latter deployments for both resin types. All samplers at Site 111SF4640 were non-detect for nodularin-R and were not included in the analysis.

3.2.4 Evaluating Integrative Performance

To determine whether adsorption rates in SPATT samplers were additive during the 14-day experiment, cumulative measurements of anatoxin-a, microcystins/nodularins, and nodularin-R for the shorter concurrent deployments were compared to the corresponding full-length deployment. For example, cumulative measurements for 4a+6b+4e and 4a+10b were compared to 14a. Averages were used for deployment schedules that were replicated. Additive concentrations of shorter deployments were expressed as a percentage of the full-length deployment, as indicated by the dashed line below (Figure 18). Overall, cumulative measurements of cyanotoxin concentrations for shorter concurrent deployments generally exceeded the concentrations of samplers deployed for the entire time period and varied depending on the resin type and deployment group combination.

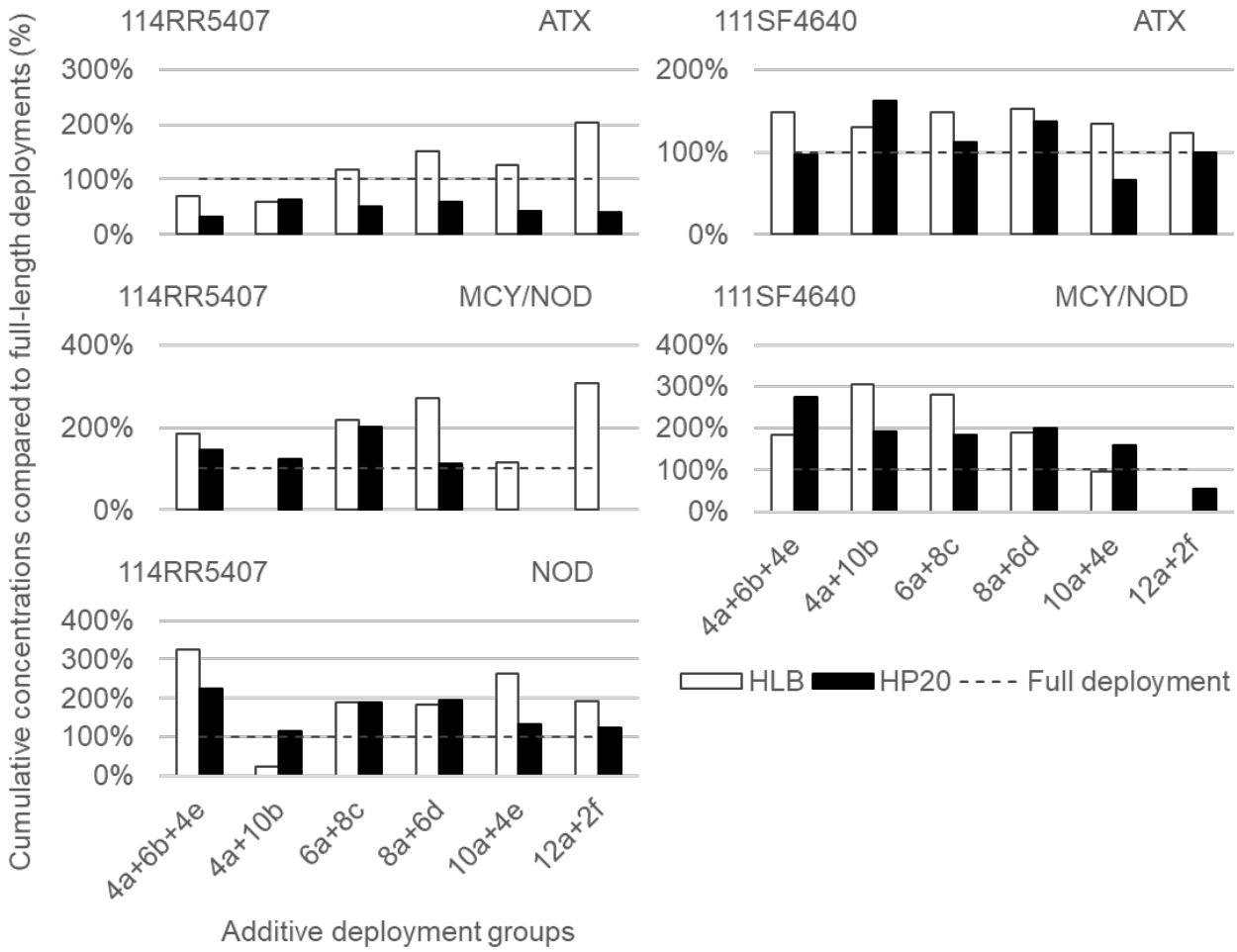

Figure 18. The percentage of anatoxin-a (ATX), microcystins/nodularins (MCY/NOD), and nodularin-R (NOD) concentrations in shorter concurrently deployed SPATT samplers compared to corresponding full-length deployments for each site in the Russian and South Fork Eel Rivers during the 14-day experiment, 2019.

To summarize the data and figure above, additive concentrations across all cyanotoxin results were counted as lower than their full-length sampler (<75%), within range of their full-length sampler (75-125%), or higher than their full-length sampler (>125%) for each site and resin type (Table 16). At Site 114RR5407, the majority of additive deployment lengths for HLB samplers were higher than the corresponding full-length sampler for all cyanotoxins, while the majority of additive deployments for HP20 samplers were lower due to low anatoxin-a concentrations. At Site 111SF4640, the majority of additive deployments were higher for both resin types. Nodularin-R was not detected by either resin types in any samplers at Site 111SF4640 and therefore is not included in the figure or table.

Table 16. Number of additive deployment lengths that are lower (<75%), within range (75-125%) or higher (>125%) than their corresponding full-length sampler for each site and resin type during the 14-day experiment in the Russian and South Fork Eel Rivers, 2019.

Site	Resin	Number of Additive Deployments								
		<75%			75-125%			>125%		
		ATX	MCY	NOD	ATX	MCY	NOD	ATX	MCY	NOD
114RR5407	HLB	2	1	1	1	1	0	3	4	5
	HP20	6	2	0	0	2	2	0	2	4
111SF4640	HLB	0	1	---	1	1	---	5	4	---
	HP20	1	1	---	3	0	---	2	5	---
Total:		9	5	1	5	4	2	10	15	9
		15			11			34		

3.2.5 Calculating Sampler Variability

To evaluate variation and repeatability in the 14-day experiment, triplicate SPATT samplers were deployed on five occasions at each site (Tables 17 and 18). The coefficient of variation was calculated for replicated samplers (CV = standard deviation / mean) to measure the level of dispersion around the mean with a higher coefficient of variation meaning greater dispersion or variability. Cyanotoxin measurements among the replicates were not constant as indicated by the differing coefficients of variation for each resin type. At Site 114RR5407, coefficients of variation for HLB and HP20 samplers ranged from 0.08-1.73 and 0.12-0.54 for anatoxin-a, 0.82-1.73 and 0.06-0.87 for microcystins/nodularins, and 0.18-0.60 and 0.12-0.23 for nodularin-R, respectively. At Site 111SF4640, coefficients of variation for HLB and HP20 samplers ranged from 0.15-0.30 and 0.01-0.73 for anatoxin-a, and 0.36-1.73 and 0.10-0.52 for microcystins/nodularins, respectively. Nodularin-R was not detected by either resin types in any samplers at Site 111SF4640 and therefore coefficients of variation were not calculated. Across all sites and cyanotoxins, the average coefficient of variation was lower in HP20 samplers (range 0.17-0.34) (Table 17) than HLB samplers (range 0.38-0.99) (Table 18). The highest variation was observed in microcystins/nodularins concentrations in HLB samplers.

Table 17. Anatoxin-a (ATX), microcystins/nodularins (MCY/NOD), and nodularin-R (NOD) concentrations for replicated SPATT samplers constructed with HLB resin in the Russian and South Fork Eel Rivers during the 14-day experiment, 2019. Summary statistics include number of samples (N), mean values, standard deviation (SD), coefficient of variation (CV), and non-detect (ND).

Site	Deployment Schedule	N	ATX (ng/g)			MCY/NOD (ng/g)			NOD (ng/g)		
			Mean	SD	CV	Mean	SD	CV	Mean	SD	CV
114RR5407	6a	3	4.9	0.7	0.14	25.1	43.4	1.73	47.6	11.6	0.24
	6b	3	1.1	1.9	1.73	59.8	57.9	0.97	54.7	10.0	0.18
	8a	3	7.9	4.5	0.57	133.0	167.9	1.26	59.5	35.4	0.60
	8c	3	4.6	1.1	0.24	164.7	134.9	0.82	61.4	30.2	0.49
	14a	3	8.1	0.6	0.08	86.6	76.4	0.88	58.1	28.5	0.49
111SF4640	6a	3	7.1	1.2	0.17	93.9	36.7	0.39	ND	---	---
	6b	3	5.9	0.9	0.15	18.5	32.1	1.73	ND	---	---
	8a	3	8.0	2.4	0.30	74.4	64.9	0.87	ND	---	---
	8c	3	7.0	1.8	0.26	141.3	50.7	0.36	ND	---	---
	14a	3	9.5	1.8	0.19	83.5	73.1	0.88	ND	---	---
				Mean CV:	0.38		**Mean CV:**	0.99		**Mean CV:**	0.40

Table 18. Anatoxin-a (ATX), microcystins/nodularins (MCY/NOD), and nodularin-R (NOD) concentrations for replicated SPATT samplers constructed with HP20 resin in the Russian and South Fork Eel Rivers during the 14-day experiment, 2019. Summary statistics include number of samples (N), mean values, standard deviation (SD), coefficient of variation (CV), and non-detect (ND).

Site	Deployment Schedule	N	ATX (ng/g)			MCY/NOD (ng/g)			NOD (ng/g)		
			Mean	SD	CV	Mean	SD	CV	Mean	SD	CV
114RR5407	6a	3	5.4	1.6	0.30	47.1	3.0	0.06	30.6	4.3	0.14
	6b	3	5.6	2.3	0.42	51.9	45.2	0.87	42.6	7.1	0.17
	8a	3	8.2	4.4	0.54	70.3	22.3	0.32	46.6	10.9	0.23
	8c	3	3.6	0.4	0.12	79.1	20.1	0.25	53.7	8.8	0.16
	14a	3	17.3	6.8	0.39	62.2	25.8	0.41	44.8	5.5	0.12
111SF4640	6a	3	2.1	0.4	0.18	107.3	11.1	0.10	ND	---	---
	6b	3	1.7	0.0	0.01	106.6	11.9	0.11	ND	---	---
	8a	3	2.9	1.2	0.41	96.4	50.3	0.52	ND	---	---
	8c	3	2.0	0.5	0.27	66.4	10.9	0.16	ND	---	---
	14a	3	3.7	2.7	0.73	94.8	29.6	0.31	ND	---	---
				Mean CV:	0.34		**Mean CV:**	0.31		**Mean CV:**	0.17

4 Discussion

In a previously released report, the Regional Water Board identified benthic cyanobacteria and cyanotoxins of concern in northern California rivers (NCRWQCB 2022). The report's monitoring recommendations include the use of SPATTs as sentinel samplers in riverine systems. Increasing cyanotoxin concentrations in SPATTs indicate upstream cyanobacterial growth and proliferation, which may result in potential health risks to the recreating public; these conditions warrant increased visual surveillance and periodic benthic mat sampling. Although SPATTs were identified as a key monitoring tool, the previous report did not identify an appropriate deployment length for SPATT samplers that would adequately characterize water column cyanotoxin concentrations. Results from this special study contribute to the understanding of how deployment length affects SPATT sampler performance in the field setting, providing the information necessary to make recommendations on appropriate deployment lengths for effective monitoring.

4.1 Study Findings

SPATT samplers in this study detected all three cyanotoxins in field settings, however, detection rates varied per cyanotoxin class. In both the 4-day and 14-day experiments, anatoxin-a was detected in all deployment groups while detections of nodularin-R and microcystins/nodularins were more variable. The experiments also revealed inconsistencies among non-detects, which occurred when a sampler without a specific cyanotoxin detection had a replicate and/or concurrent sampler with a detection. Inconsistent non-detects were highest when measuring microcystins/nodularins; this finding is counter to expectations since microcystins have been shown to reach equilibrium in hours (Kudela 2011) compared to days for anatoxins (Bouma-Gregson et al. 2018, Kudela 2020). Therefore, microcystins were thought to respond more quickly to environmental concentrations than anatoxin, specifically in HP20 resin. In the 14-day experiment, rates of inconsistent non-detects across all cyanotoxins were lowest in 2-, 4- and 8-day deployments, indicating that longer deployments may result in less consistent detections. SPATTs with HP20 resin also had higher detection rates and more consistent non-detections, suggesting that this resin is preferable to the HLB alternative. However, it cannot be ruled out that variation in detections may have been due to unknown factors such as resin failure, inadvertent field error, the extraction efficiency in the laboratory, or fine-scale differences in water hydraulics around each SPATT that results in the delivery of different amounts of cyanotoxins to a specific sampler.

Results from the 4-day experiment demonstrated that SPATTs can adsorb cyanotoxins within one day. Some linear regression models for both experiments showed a positive relationship between deployment length and cyanotoxin concentrations (e.g., anatoxin-a), however, there was considerable variance in the relationships between SPATT concentration and deployment length. When comparing deployment groups, there were instances of longer deployment groups having significantly higher concentrations than

shorter deployment groups, however, these findings were not always consistent among cyanotoxin classes, sites, or resin types. Indeed, environmental factors such as flow, turbidity, biofilm formation, and variation in cyanobacteria assemblages and cyanotoxin concentrations need to be considered as these are likely to vary from site to site and therefore impact SPATT measurements (Kudela 2020). Despite these differences, results from this study suggest that initial adsorption can occur rapidly, and longer deployment lengths (e.g., 14-day) may not provide additionally relevant information, especially when attempting to characterize current cyanotoxin conditions.

Cumulative concentrations of shorter deployments were generally higher than their corresponding full-length sampler. These results suggest that SPATTs are not perfectly kinetic, i.e., zero-sink samplers that do not desorb toxins from the SPATT resin (Kudela 2017), but rather adsorb and desorb toxins until reaching equilibrium with water column cyanotoxin concentrations. As described in a previous study, cyanotoxins adsorbed within the SPATT sampler eventually reach equilibrium with ambient concentrations in the water column (Kudela 2020). In this study, cyanotoxins rapidly adsorbed within the first day, followed by slower daily increases over longer deployments; this is likely due to the longer deployments nearing equilibrium. Another study evaluating SPATT performance observed a similar saturation or equilibrium point where anatoxin concentrations were not significantly different after being deployed for four hours (Wood et al. 2011).

In the 4-day experiment, there were instances where cyanotoxin increases in single-day deployments corresponded with increases in longer concurrent deployments (Figure 8). This observation mostly applied to anatoxin-a since microcystins/nodularins and nodularin-R detections and measurements were more variable. There was some evidence that decreases in single-day anatoxin-a concentrations also corresponded with decreases in longer concurrent deployments, although the decrease in longer deployments had a delayed response. Data for desorption are limited in this study, however, a study conducted under laboratory conditions demonstrated that saturated SPATT samplers deployed in low levels of ambient cyanotoxins will decrease in concentration over a four-day period (Kudela 2020). These combined observations suggest that SPATTs are able to capture fluctuations or pulses in cyanotoxin production, however, cyanotoxins will begin to desorb from the sampler as ambient water column concentrations decline. Accordingly, cyanotoxin concentrations in SPATTs likely reflect conditions that were present towards the end of the deployment since the sampler is constantly equilibrating to changing ambient concentrations.

Variation among replicated SPATT samplers differed depending on cyanotoxin and resin type. In both experiments, coefficients of variation in replicated samplers were comparable for anatoxin-a and nodularin-R measurements while they were higher in microcystins/nodularins measurements. These results suggest that adsorption of anatoxin-a and nodularin-R may be more reliable than microcystins/nodularins. Alternatively, because microcystins/nodularins were measured by ELISA, while

anatoxin-a and nodularin-R measured by LCMS, the differences in variation could be an artifact of the analytical methods and not driven by the adsorption-desorption kinetics between the SPATT resin and the cyanotoxin molecules. LCMS measures specific congeners such as anatoxin-a and nodularin-R, and, therefore, may provide more precise results than ELISA, which measures groups of congeners such as microcystins/nodularins that can be more subject to matrix effects and cross reactivities.

In the 14-day experiment, overall results suggest that HLB samplers may adsorb cyanotoxins at greater concentrations than HP20 samplers, however, significant differences in resin types varied per deployment group and site. In another study, HLB samplers adsorbed cyanotoxins more readily and at a faster rate under laboratory conditions, however, differences between HLB and HP20 samplers in a field setting were not as significant (Kudela 2020). Despite potentially higher adsorption rates in HLB samplers, this study demonstrated that samplers constructed with HP20 resin were less variable across all cyanotoxin classes, suggesting that this resin can more reliably adsorb cyanotoxins than HLB resin. Higher adsorption rates and actual concentrations captured by SPATTs are less significant when interpreting data trends to document potential biomass growth and public health risks. Instead, the reliability of SPATTs adsorbing cyanotoxins is of greater importance to a public health monitoring program.

4.2 Monitoring Recommendations

Based on the results of this special study, the Regional Water Board recommends a four- to eight-day deployment length to characterize cyanotoxin concentrations in a riverine system. This time period exhibited less inconsistencies among non-detects, however, results demonstrate that inconsistent non-detects can occur regardless of deployment length. The four-day deployment also provides more time for anatoxin-a, which adsorbs to HP20 resin slower than microcystins/nodularins, to concentrate on the SPATT resin. This recommendation is similar to results from laboratory experiments that support a greater than two-day deployment: Kudela (2020) recommends a four-day deployment as SPATT samplers were documented to equilibrate to laboratory-controlled anatoxin concentrations during this time; Bouma-Gregson et al. (2018) showed SPATTs equilibrating to laboratory-controlled anatoxin concentrations between two to three days. Kudela (2020) also suggested that deployments longer than 8 days are more likely to equilibrate to conditions that are present at the end of the deployment period. If longer deployments are used, quantitative comparisons between SPATT samplers become more challenging due to increasingly complex adsorption and desorption kinetics that occur as the deployment length increases. Weekly or seven-day deployments are recommended as optimal since these are logistically convenient for routine monitoring, i.e., deployment and retrieval can be scheduled on the same day each week.

This study compared adsorption among three cyanotoxin classes and between two commercially available resins. Given the higher detection rates, lower rates of inconsistent non-detects, and less variability among replicated samplers, the Regional

Water Board is confident in the measurements of anatoxin-a concentrations in SPATTs. The ability to accurately characterize anatoxin-a is critical since this potent neurotoxin has been implicated in several dog deaths in the North Coast Region. Regarding resin type, the Regional Water Board recommends using HP20 resin when constructing samplers due to its higher detection rates, lower rates of inconsistent non-detects, and lower variability among replicates. HP20 resin was also recommended by Zhao et al. (2013) and Kudela (2011, 2020).

As seen with the numerous non-detects in discrete water grab samples during the 4-day experiment, integrative SPATT samplers remain an effective tool for documenting low levels of ambient cyanotoxins. Previous research also demonstrated that SPATTs detected cyanotoxins at a higher rate than water grab samples (Kudela 2011, Wood et al. 2011, NCRWQCB 2022). The Regional Water Board continues to support and recommend the use of SPATTs as sentinel samplers to determine when cyanotoxins are present and when subsequent visual surveillance and benthic mat sampling are needed. Regardless of resin choice or deployment length, the Regional Water Board recommends consistent methodology when documenting and determining SPATT cyanotoxin trends in a riverine setting. Results derived from regular and consistent monitoring can provide waterbody managers and public health officials with the information necessary to develop and implement response scenarios for the protection of public health.

4.3 Recommendations for Future Studies

This study identifies inconsistent non-detects as SPATTs without cyanotoxin detections that have replicates or concurrent samplers with cyanotoxin detections. These results were included in the report to illustrate real-world variability in SPATT performance, i.e., the detections among cyanotoxin classes, deployment length, and resin type. Although inconsistent non-detects were identified, determining the causal factors of non-detection is beyond the scope of this study. Error and uncertainty can be introduced in many areas of the study, including error in field methods, error with extraction efficiencies in the laboratory, and confounding environmental factors such as hydraulics and fouling. Future studies could explore the causes of non-detects, and in doing so, identify whether non-detects reflect actual absence of cyanotoxins, or if there are instances where samplers fail and should be considered false negatives.

This study also sheds light on potential differences between ELISA and LCMS results. As mentioned previously, ELISA measures groups of cyanotoxin congeners while LCMS targets specific congeners. In this study, similar trends were observed across all three cyanotoxins, however, variances among replicated samplers were lower for anatoxin-a and nodularin-R, suggesting that congener-specific LCMS my provide more precise measurements than ELISA. Future studies could determine the extent of differences between the two laboratory techniques and how any differences may affect the interpretation of SPATT results.

5 References

Bouma-Gregson, K., Kudela, R. M., and Power, M. E. (2018). Widespread anatoxin-a detection in benthic cyanobacterial mats throughout a river network. *PLOS ONE* 13, e0197669.

Chorus, I., and Welker, M. (2021). Toxic Cyanobacteria in Water: A Guide to their Public Health Consequences, Monitoring and Management. CRC Press on behalf of the World Health Organization, Geneva, CH.

Conklin, K. Y., Stancheva, R., Otten, T. G., Fadness, R., Boyer, G. L., Read, B., et al. (2020). Molecular and morphological characterization of a novel dihydroanatoxin-a producing Microcoleus species (Cyanobacteria) from the Russian River, California, USA. *Harmful Algae* 93, 101767.

Dittmann, E., Fewer, D.P. & Neilan, B.A. (2013). Cyanobacterial toxins: biosynthetic routes and evolutionary roots. *FEMS Microbiology Reviews*, 37, 23–43.

Gibble, C.M. & Kudela, R.M. (2014). Detection of persistent microcystin toxins at the land–sea interface in Monterey Bay, California. *Harmful Algae*, 39, 146–153.

Huisman, J., Codd, G.A., Paerl, H.W., Ibelings, B.W., Verspagen, J.M.H. & Visser, P.M. (2018). Cyanobacterial blooms. *Nat Rev Microbiol*, 16, 471–483.

Kudela, R.M. (2011). Characterization and deployment of Solid Phase Adsorption Toxin Tracking (SPATT) resin for monitoring of microcystins in fresh and saltwater. *Harmful Algae*, 11, 117–125.

Kudela, R.M. (2017). Passive Sampling for Freshwater and Marine Algal Toxins. In: *Comprehensive Analytical Chemistry*. Elsevier, pp. 379–409.

Kudela, R.M. (2020). Research and develop methods for toxin monitoring by passive samplers. Surface Water Ambient Monitoring Program, State Water Resources Control Board, Sacramento, California.

Lane, J.Q., Roddam, C.M., Langlois, G.W., and Kudela, R.M. (2010). Application of Solid Phase Adsorption Toxin Tracking (SPATT) for field detection of the hydrophilic phycotoxins domoic acid and saxitoxin in coastal California. *Limnology and Oceanography: Methods*, 8, 645-660.

MacKenzie, L., Beuzenberg, V., Holland, P., McNabb, P. & Selwood, A. (2004). Solid phase adsorption toxin tracking (SPATT): a new monitoring tool that simulates the biotoxin contamination of filter feeding bivalves. *Toxicon*, 44, 901–918.

NCRWQCB. (2022). Benthic Cyanobacteria and Cyanotoxin Monitoring in Northern California Rivers, 2016-2019. Freshwater Harmful Algal Bloom Monitoring and Response Program, North Coast Regional Water Quality Control Board, Santa Rosa, California.

Puschner, B., Hoff, B., and Tor, E. R. (2008). Diagnosis of Anatoxin-a Poisoning in Dogs from North America. *Journal of Veterinary Diagnostic Investigation* 20, 89–92.

Quiblier, C., Mark, H., Aurélie, V. & Jean-François, H. (2013). A review of current knowledge on toxic benthic freshwater cyanobacteria – Ecology, toxin production and risk management. *Water Research*, 47, 5464–5479.

Roué, M., Darius, H.T. & Chinain, M. (2018). Solid Phase Adsorption Toxin Tracking (SPATT) Technology for the Monitoring of Aquatic Toxins: A Review. *Toxins*, 10, 167.

Wood, S.A., Biessy, L. & Puddick, J. (2018). Anatoxins are consistently released into the water of streams with *Microcoleus autumnalis*-dominated (Cyanobacteria) proliferations. *Harmful Algae*, 80, 88–95.

Wood, S.A., Holland, P.T. & MacKenzie, L. (2011). Development of solid phase adsorption toxin tracking (SPATT) for monitoring anatoxin-a and homoanatoxin-a in river water. *Chemosphere*, 82, 888–894.

Wood, S.A., Kelly, L.T., Bouma-Gregson, K., Humbert, J., Laughinghouse, H.D., Lazorchak, J., *et al.* (2020). Toxic benthic freshwater cyanobacterial proliferations: Challenges and solutions for enhancing knowledge and improving monitoring and mitigation. *Freshw. Biol.*, 65, 1824–1842.,

Zhao, H., Qiu, J., Fan, H., and Li, A. (2013). Mechanism and application of solid phase adsorption toxin tracking for monitoring microcystins. *Journal of Chromatography A* 1300, 159–164.

6 Appendices

Appendix 1. Anatoxin-a (ATX), microcystins/nodularins (MCY/NOD), and nodularin-R (NOD) concentrations in SPATT samplers constructed with HP20 resin during the 4-day experiment in the Navarro and South Fork Eel Rivers, 2019.

River	Site	Schedule	Replicate	Resin	Deploy Date	Retrieval Date	LCMS ATX (ng/g)	LCMS NOD (ng/g)	ELISA MCY/NOD (ng/g)
Navarro	113NA9990	1a	1	HP20	8/26/2019	8/27/2019	25.21	11.66	30.58
Navarro	113NA9990	1b	1	HP20	8/27/2019	8/28/2019	38.98	12.58	23.08
Navarro	113NA9990	1c	1	HP20	8/28/2019	8/29/2019	19.57	9.74	ND
Navarro	113NA9990	1c	2	HP20	8/28/2019	8/29/2019	16.99	15.51	ND
Navarro	113NA9990	1d	1	HP20	8/29/2019	8/30/2019	15.52	9.36	ND
Navarro	113NA9990	2a	1	HP20	8/26/2019	8/28/2019	57.27	13.44	28.17
Navarro	113NA9990	2d	1	HP20	8/28/2019	8/30/2019	14.84	13.30	35.25
Navarro	113NA9990	2d	2	HP20	8/28/2019	8/30/2019	12.08	15.83	ND
Navarro	113NA9990	2d	3	HP20	8/28/2019	8/30/2019	20.25	12.26	50.00
Navarro	113NA9990	3a	1	HP20	8/26/2019	8/29/2019	63.79	15.87	25.83
Navarro	113NA9990	4a	1	HP20	8/26/2019	8/30/2019	35.01	17.24	33.50
Navarro	113NA9990	4a	2	HP20	8/26/2019	8/30/2019	31.78	16.77	41.67
Navarro	113NA9990	4a	3	HP20	8/26/2019	8/30/2019	49.82	13.48	36.92
SF Eel	111SF2423	1a	1	HP20	8/26/2019	8/27/2019	9.16	ND	ND
SF Eel	111SF2423	1b	1	HP20	8/27/2019	8/28/2019	8.28	ND	ND
SF Eel	111SF2423	1c	1	HP20	8/28/2019	8/29/2019	5.40	6.56	15.42
SF Eel	111SF2423	1d	1	HP20	8/29/2019	8/30/2019	6.41	3.26	34.42
SF Eel	111SF2423	2a	1	HP20	8/26/2019	8/28/2019	14.57	ND	ND
SF Eel	111SF2423	2a	2	HP20	8/26/2019	8/28/2019	12.33	ND	14.67
SF Eel	111SF2423	2a	3	HP20	8/26/2019	8/28/2019	18.21	ND	ND
SF Eel	111SF2423	2d	1	HP20	8/28/2019	8/30/2019	10.27	2.92	15.42
SF Eel	111SF2423	3a	1	HP20	8/26/2019	8/29/2019	15.88	ND	ND
SF Eel	111SF2423	4a	1	HP20	8/26/2019	8/30/2019	6.33	3.12	15.92

River	Site	Schedule	Replicate	Resin	Deploy Date	Retrieval Date	LCMS ATX (ng/g)	LCMS NOD (ng/g)	ELISA MCY/NOD (ng/g)
SF Eel	111SF2423	4a	2	HP20	8/26/2019	8/30/2019	9.80	1.83	ND
SF Eel	111SF2423	4a	3	HP20	8/26/2019	8/30/2019	11.48	1.85	27.50
SF Eel	111SF4640	1a	1	HP20	8/26/2019	8/27/2019	438.46	10.24	43.00
SF Eel	111SF4640	1a	2	HP20	8/26/2019	8/27/2019	411.99	15.49	ND
SF Eel	111SF4640	1b	1	HP20	8/27/2019	8/28/2019	453.12	3.47	ND
SF Eel	111SF4640	1c	1	HP20	8/28/2019	8/29/2019	280.24	5.41	ND
SF Eel	111SF4640	1c	2	HP20	8/28/2019	8/29/2019	253.26	4.58	ND
SF Eel	111SF4640	1d	1	HP20	8/29/2019	8/30/2019	214.25	3.89	ND
SF Eel	111SF4640	2a	1	HP20	8/26/2019	8/28/2019	545.13	ND	ND
SF Eel	111SF4640	2d	1	HP20	8/28/2019	8/30/2019	307.51	13.39	22.25
SF Eel	111SF4640	2d	2	HP20	8/28/2019	8/30/2019	320.11	14.56	ND
SF Eel	111SF4640	3a	1	HP20	8/26/2019	8/29/2019	323.37	ND	ND
SF Eel	111SF4640	4a	1	HP20	8/26/2019	8/30/2019	1093.29	23.47	49.50
SF Eel	111SF4640	4a	2	HP20	8/26/2019	8/30/2019	646.15	15.55	19.92
SF Eel	111SF4640	4a	3	HP20	8/26/2019	8/30/2019	501.68	14.53	26.92
SF Eel	111SF6856	1a	1	HP20	8/26/2019	8/27/2019	---	39.13	75.33
SF Eel	111SF6856	1b	1	HP20	8/27/2019	8/28/2019	---	59.65	105.08
SF Eel	111SF6856	1c	1	HP20	8/28/2019	8/29/2019	5.27	103.99	304.58
SF Eel	111SF6856	1d	1	HP20	8/29/2019	8/30/2019	4.24	52.57	81.42
SF Eel	111SF6856	2a	1	HP20	8/26/2019	8/28/2019	4.47	109.11	372.58
SF Eel	111SF6856	2d	1	HP20	8/28/2019	8/30/2019	4.83	94.51	195.67
SF Eel	111SF6856	3a	1	HP20	8/26/2019	8/29/2019	5.82	67.81	87.25
SF Eel	111SF6856	4a	1	HP20	8/26/2019	8/30/2019	8.59	97.43	223.08

Appendix 2. Anatoxin-a (ATX), microcystins/nodularins (MCY/NOD), and nodularin-R (NOD) concentrations in SPATT samplers constructed with HLB and HP20 resins during the 14-day experiment in the Russian and South Fork Eel Rivers, 2019.

River	Site	Schedule	Replicate	Resin	Deploy Date	Retrieval Date	LCMS ATX (ng/g)	LCMS NOD (ng/g)	ELISA MCY/NOD (ng/g)
Russian	114RR5407	4a	1	HLB	9/27/2019	10/1/2019	ND	13.30	ND
Russian	114RR5407	6a	1	HLB	9/27/2019	10/3/2019	5.29	52.95	75.20
Russian	114RR5407	6a	2	HLB	9/27/2019	10/3/2019	5.31	34.34	ND
Russian	114RR5407	6a	3	HLB	9/27/2019	10/3/2019	4.13	55.54	ND
Russian	114RR5407	8a	1	HLB	9/27/2019	10/5/2019	6.28	25.42	ND
Russian	114RR5407	8a	2	HLB	9/27/2019	10/5/2019	12.93	56.82	77.21
Russian	114RR5407	8a	3	HLB	9/27/2019	10/5/2019	4.45	96.11	321.67
Russian	114RR5407	10a	1	HLB	9/27/2019	10/7/2019	5.71	32.29	ND
Russian	114RR5407	12a	1	HLB	9/27/2019	10/9/2019	7.74	80.31	192.40
Russian	114RR5407	14a	1	HLB	9/27/2019	10/11/2019	7.37	88.66	ND
Russian	114RR5407	14a	2	HLB	9/27/2019	10/11/2019	8.49	53.37	115.19
Russian	114RR5407	14a	3	HLB	9/27/2019	10/11/2019	8.47	32.34	144.61
Russian	114RR5407	10d	1	HLB	10/1/2019	10/11/2019	4.83	ND	ND
Russian	114RR5407	8d	1	HLB	10/3/2019	10/11/2019	4.16	49.10	92.05
Russian	114RR5407	8d	2	HLB	10/3/2019	10/11/2019	3.71	39.37	81.74
Russian	114RR5407	8d	3	HLB	10/3/2019	10/11/2019	5.81	95.85	320.41
Russian	114RR5407	6d	1	HLB	10/5/2019	10/11/2019	4.36	47.65	102.36
Russian	114RR5407	4d	1	HLB	10/7/2019	10/11/2019	4.54	120.67	100.60
Russian	114RR5407	2d	1	HLB	10/9/2019	10/11/2019	8.70	30.33	73.94
Russian	114RR5407	6b	1	HLB	10/1/2019	10/7/2019	ND	43.63	ND
Russian	114RR5407	6b	2	HLB	10/1/2019	10/7/2019	3.21	63.16	63.63
Russian	114RR5407	6b	3	HLB	10/1/2019	10/7/2019	ND	57.39	115.69
Russian	114RR5407	4a	1	HP20	9/27/2019	10/1/2019	ND	25.30	39.23
Russian	114RR5407	6a	1	HP20	9/27/2019	10/3/2019	4.84	28.44	50.47

River	Site	Schedule	Replicate	Resin	Deploy Date	Retrieval Date	LCMS ATX (ng/g)	LCMS NOD (ng/g)	ELISA MCY/NOD (ng/g)
Russian	114RR5407	6a	2	HP20	9/27/2019	10/3/2019	7.22	35.52	45.27
Russian	114RR5407	6a	3	HP20	9/27/2019	10/3/2019	4.08	27.69	45.44
Russian	114RR5407	8a	1	HP20	9/27/2019	10/5/2019	13.37	42.50	63.55
Russian	114RR5407	8a	2	HP20	9/27/2019	10/5/2019	5.92	38.44	52.14
Russian	114RR5407	8a	3	HP20	9/27/2019	10/5/2019	5.44	59.00	95.23
Russian	114RR5407	10a	1	HP20	9/27/2019	10/7/2019	7.24	26.94	ND
Russian	114RR5407	12a	1	HP20	9/27/2019	10/9/2019	3.41	30.41	ND
Russian	114RR5407	14a	1	HP20	9/27/2019	10/11/2019	13.35	49.85	38.06
Russian	114RR5407	14a	2	HP20	9/27/2019	10/11/2019	25.19	45.72	89.37
Russian	114RR5407	14a	3	HP20	9/27/2019	10/11/2019	13.49	38.97	59.19
Russian	114RR5407	10d	1	HP20	10/1/2019	10/11/2019	10.95	26.06	37.89
Russian	114RR5407	8d	1	HP20	10/3/2019	10/11/2019	3.31	46.10	64.05
Russian	114RR5407	8d	2	HP20	10/3/2019	10/11/2019	4.07	51.78	71.43
Russian	114RR5407	8d	3	HP20	10/3/2019	10/11/2019	3.31	63.28	101.94
Russian	114RR5407	6d	1	HP20	10/5/2019	10/11/2019	2.09	40.98	ND
Russian	114RR5407	4d	1	HP20	10/7/2019	10/11/2019	ND	33.07	ND
Russian	114RR5407	2d	1	HP20	10/9/2019	10/11/2019	3.79	24.83	ND
Russian	114RR5407	6b	1	HP20	10/1/2019	10/7/2019	2.89	34.59	ND
Russian	114RR5407	6b	2	HP20	10/1/2019	10/7/2019	7.14	44.90	83.16
Russian	114RR5407	6b	3	HP20	10/1/2019	10/7/2019	6.71	48.18	72.43
SF Eel	111SF4640	4a	1	HLB	9/27/2019	10/1/2019	4.29	ND	133.80
SF Eel	111SF4640	6a	1	HLB	9/27/2019	10/3/2019	6.65	ND	76.71
SF Eel	111SF4640	6a	2	HLB	9/27/2019	10/3/2019	8.45	ND	136.06
SF Eel	111SF4640	6a	3	HLB	9/27/2019	10/3/2019	6.13	ND	68.91
SF Eel	111SF4640	8a	1	HLB	9/27/2019	10/5/2019	9.68	ND	119.46
SF Eel	111SF4640	8a	2	HLB	9/27/2019	10/5/2019	8.99	ND	103.62
SF Eel	111SF4640	8a	3	HLB	9/27/2019	10/5/2019	5.28	ND	ND
SF Eel	111SF4640	10a	1	HLB	9/27/2019	10/7/2019	8.77	ND	79.98

River	Site	Schedule	Replicate	Resin	Deploy Date	Retrieval Date	LCMS ATX (ng/g)	LCMS NOD (ng/g)	ELISA MCY/NOD (ng/g)
SF Eel	111SF4640	12a	1	HLB	9/27/2019	10/9/2019	7.31	ND	ND
SF Eel	111SF4640	14a	1	HLB	9/27/2019	10/11/2019	8.17	ND	ND
SF Eel	111SF4640	14a	2	HLB	9/27/2019	10/11/2019	8.75	ND	136.06
SF Eel	111SF4640	14a	3	HLB	9/27/2019	10/11/2019	11.54	ND	114.43
SF Eel	111SF4640	10d	1	HLB	10/1/2019	10/11/2019	8.01	ND	119.97
SF Eel	111SF4640	8d	1	HLB	10/3/2019	10/11/2019	6.77	ND	92.05
SF Eel	111SF4640	8d	2	HLB	10/3/2019	10/11/2019	5.29	ND	138.33
SF Eel	111SF4640	8d	3	HLB	10/3/2019	10/11/2019	8.94	ND	193.40
SF Eel	111SF4640	6d	1	HLB	10/5/2019	10/11/2019	6.48	ND	82.74
SF Eel	111SF4640	4d	1	HLB	10/7/2019	10/11/2019	3.91	ND	ND
SF Eel	111SF4640	2d	1	HLB	10/9/2019	10/11/2019	4.35	ND	ND
SF Eel	111SF4640	6b	1	HLB	10/1/2019	10/7/2019	5.70	ND	55.58
SF Eel	111SF4640	6b	2	HLB	10/1/2019	10/7/2019	5.12	ND	ND
SF Eel	111SF4640	6b	3	HLB	10/1/2019	10/7/2019	6.83	ND	ND
SF Eel	111SF4640	4a	1	HP20	9/27/2019	10/1/2019	1.88	ND	98.92
SF Eel	111SF4640	6a	1	HP20	9/27/2019	10/3/2019	1.99	ND	96.74
SF Eel	111SF4640	6a	2	HP20	9/27/2019	10/3/2019	1.81	ND	118.88
SF Eel	111SF4640	6a	3	HP20	9/27/2019	10/3/2019	2.55	ND	106.30
SF Eel	111SF4640	8a	1	HP20	9/27/2019	10/5/2019	4.14	ND	90.37
SF Eel	111SF4640	8a	2	HP20	9/27/2019	10/5/2019	1.82	ND	49.29
SF Eel	111SF4640	8a	3	HP20	9/27/2019	10/5/2019	2.66	ND	149.39
SF Eel	111SF4640	10a	1	HP20	9/27/2019	10/7/2019	2.47	ND	95.23
SF Eel	111SF4640	12a	1	HP20	9/27/2019	10/9/2019	3.69	ND	52.14
SF Eel	111SF4640	14a	1	HP20	9/27/2019	10/11/2019	6.80	ND	76.29
SF Eel	111SF4640	14a	2	HP20	9/27/2019	10/11/2019	2.66	ND	79.14
SF Eel	111SF4640	14a	3	HP20	9/27/2019	10/11/2019	1.68	ND	128.94
SF Eel	111SF4640	10d	1	HP20	10/1/2019	10/11/2019	4.13	ND	82.66
SF Eel	111SF4640	8d	1	HP20	10/3/2019	10/11/2019	1.43	ND	78.97

River	Site	Schedule	Replicate	Resin	Deploy Date	Retrieval Date	LCMS ATX (ng/g)	LCMS NOD (ng/g)	ELISA MCY/NOD (ng/g)
SF Eel	111SF4640	8d	2	HP20	10/3/2019	10/11/2019	2.25	ND	59.02
SF Eel	111SF4640	8d	3	HP20	10/3/2019	10/11/2019	2.46	ND	61.20
SF Eel	111SF4640	6d	1	HP20	10/5/2019	10/11/2019	2.23	ND	93.73
SF Eel	111SF4640	4d	1	HP20	10/7/2019	10/11/2019	ND	ND	54.16
SF Eel	111SF4640	2d	1	HP20	10/9/2019	10/11/2019	ND	ND	ND
SF Eel	111SF4640	6b	1	HP20	10/1/2019	10/7/2019	1.68	ND	120.22
SF Eel	111SF4640	6b	2	HP20	10/1/2019	10/7/2019	1.71	ND	101.61
SF Eel	111SF4640	6b	3	HP20	10/1/2019	10/7/2019	1.73	ND	98.09