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Characterization and deployment of Solid Phase Adsorption Toxin Tracking (SPATT) resin for monitoring of microcystins in fresh and saltwater

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ABSTRACT

Fresh and brackish water cyanobacterial blooms and their associated toxins appear to be increasing globally. Current sampling methodologies for cyanotoxins typically involve point (grab) samples, and are subject to variability due to spatial and temporal heterogeneity, hydrological conditions, and the presence or absence of surface accumulations (scums) of algae. To overcome some of these issues, passive samplers including Solid Phase Adsorption Toxin Tracking (SPATT) and Polar Organic Compound Integrative Samplers (POCIS) have been used for primarily marine phycotoxins with more limited application to freshwater toxins. In this study SPATT was evaluated in both the lab and the field for use as an integrative sampler for microcystins, deployed in freshwater using DIAION HP20 resin. HP20 exhibited excellent adsorption and recovery characteristics for microcystin-LR, -YR, -LA, and -RR. Approximately weekly deployments of SPATT in Pinto Lake, CA were conducted for 16 months and compared to traditional (grab) samples. SPATT proved to be robust, detecting microcystins during every deployment in contrast to the grab samples, 42% of which were below the limit of detection using liquid chromatography–mass spectrometry for microcystin-LR. A simple canonical correlation model was built to determine if toxin concentrations co-varied with environmental parameters such as water temperature, nutrient concentrations, chlorophyll *a*, rainfall, or other easily obtained variables. The best individual correlate to toxin concentration was total biomass (chlorophyll *a*), while the first principal axis of the canonical correlation included chlorophyll *a* and total dissolved nitrogen as statistically significant variables. Overall, SPATT proved to be a useful adjunct or replacement for traditional grab samples.

1. Introduction

Cyanobacterial blooms and their associated toxins have become increasingly problematic globally (Chen et al., 1993; Dawson, 1998; Amorim and Vasconcelos, 1999; Domingos et al., 1999; Lehman et al., 2005; Guo, 2007; Paerl and Huisman, 2008). *Microcystis aeruginosa* in particular is considered a cyanobacterial harmful algal bloom (CHAB) organism because it can impede recreational use of waterbodies, reduce aesthetics, lower dissolved oxygen concentration, and cause taste and odor problems in drinking water, as well as produce microcystins, powerful hepatotoxins associated with liver cancer and tumors in humans and wildlife (Carmichael, 2001). Extensive *Microcystis* blooms with toxin production occur during summer and fall in impaired waterways in Washington, Oregon and California (Gilroy et al., 2000; Johnston and Jacoby, 2003) and *Microcystis* contamination has been documented at the marine outflows of the Klamath and San Francisco estuaries (Lehman et al., 2005; Fetcho, 2007) as well as from river inputs to Monterey Bay (Miller et al., 2010). The recently documented direct impact to the threatened California Sea Otter (*Enhydra lutris*) has also promoted these blooms and toxins from predominantly a freshwater issue to potentially a land–sea problem, with concomitant risk because of the lack of monitoring in brackish and marine waters (Miller et al., 2010).

Microcystis growth and toxin production has been linked to high nutrient concentrations, increased salinity, warm temperatures, increased vertical stratification of lakes, summer droughts and increased light intensity; all of these factors can be exacerbated by global climate change (Zehnder and Gorham, 1960; Welker and Steinberg, 2000; Guo, 2007; Paerl and Huisman, 2008; Davis et al., 2009). Cyanobacteria such as *Microcystis* can exploit these conditions by accumulating in dense surface blooms that "shade out" nontoxic phytoplankton, thereby increasing local water temperatures through light absorption and creating a positive feedback loop leading to more blooms (Paerl and Huisman, 2008).

Microcystin and other biotoxins can exert their effects in regions that are remote from sources of toxin production and can bio-accumulate in invertebrates and fish, suggesting efficient

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means for exposure to freshwater-derived toxins downstream as well as at the land–sea interface (Garcia et al., 2010; Lehman et al., 2010; Miller et al., 2010). Given the severe and ubiquitous nature of this problem in freshwater habitats and potentially coastal marine systems, surveillance and monitoring is critical. Traditional monitoring programs for phycotoxins typically rely on discrete sampling ("grab" samples) from a particular site or sites, sometimes augmented with automated sampling systems. Such methods are inherently biased if the sampling does not capture the spatial and temporal variability of the system due to (e.g.) behavioral adaptations of the algae such as vertical migration, hydrologic or circulation effects, and ephemeral or episodic events. Furthermore, grab sampling may underestimate the presence of low levels of toxins if the sampling protocol does not include pre-concentration and/or if the toxin concentrations are below the analytical limit of detection.

To overcome some of these issues, various types of passive integrated samplers have been developed and deployed for environmental contaminants and toxins (see reviews in Górecki and Namiésnik, 2002; Kot-Wasik et al., 2007; Seethapathy et al., 2008; MacKenzie, 2010). Solid Phase Adsorption Toxin Tracking (SPATT; MacKenzie et al., 2004) in particular has been widely adopted for the detection of marine phycotoxins (MacKenzie et al., 2004; Lane et al., 2010; MacKenzie, 2010). For freshwater and brackish systems, both SPATT and Polar Organic Compound Integrative Samplers (POCIS) have been deployed successfully to detect or monitor microcystins (Kohoutek et al., 2008, 2010; Miller et al., 2010) and anatoxins (Wood et al., 2011), but characterization and adoption of SPATT for these systems has been much more limited.

Prior to this study, SPATT deployments with DIAON HP20 have been used extensively in marine waters, primarily targeting lipophilic algal toxins and the water-soluble compound domoic acid (cf. MacKenzie et al., 2004; MacKenzie, 2010; Lane et al., 2010). A limited analysis in marine waters using both field deployments and tank experiments (Miller et al., 2010) also documented the potential for detection of microcystins from HP20 SPATT, but the efficacy of SPATT was not fully evaluated. This study demonstrates the potential to use SPATT with a single resin (DIAON HP20) to detect multiple phycotoxins from various environments.

The aims of this study were to characterize SPATT using the resin DIAION HP20 for passive sampling of microcystins in freshwater, and to demonstrate the applicability of SPATT sampling compared to traditional grab sampling using a known CHAB "hotspot", Pinto Lake, California (Miller et al., 2010). Secondarily, the data collected from this study were used to determine whether there are any easily measured environmental correlates that could be used to predict toxin loads for this system.

2. Materials and methods

2.1. Study area

Pinto Lake is a shallow natural lake located 8.3 km inland from Monterey Bay (Fig. 1). It is connected to the Pacific Ocean through an overflow drainage system into Corralitos Creek, which in turn

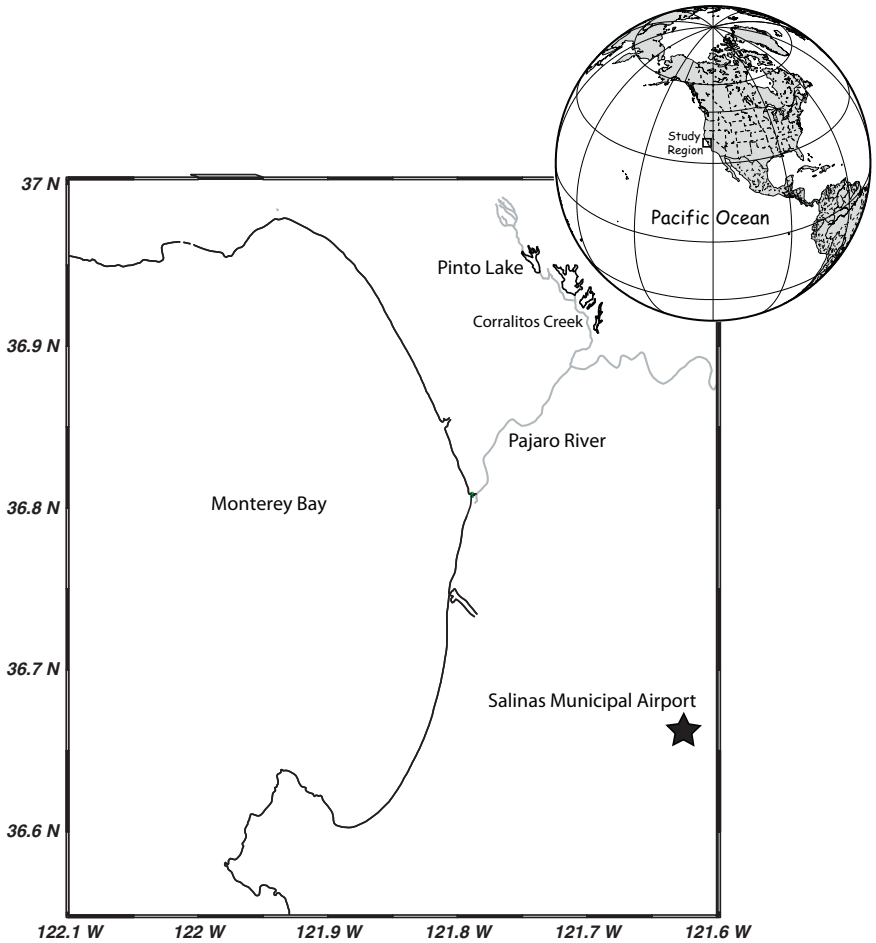

Fig. 1. Map of Monterey Bay, California showing the location of Pinto Lake, Corralitos Creek, and the Pajaro River. The Salinas Municipal Airport (star) is also indicated.