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Detection of persistent microcystin toxins at the land–sea interface in Monterey Bay, California

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ABSTRACT

Blooms of toxin-producing *Microcystis aeruginosa* occur regularly in freshwater systems throughout California, but until recently potential impacts in the coastal ocean have been largely ignored. Twenty-one sites in and around Monterey Bay were surveyed for evidence of microcystin toxin (2010–2011) at the land–sea interface. Following this initial survey four major watersheds in the Monterey Bay area were surveyed (2011–2013) for microcystin concentration, nutrients, alkalinity and water temperature to identify potential environmental factors correlated with the abundance of microcystin at the land–sea interface. During the first year microcystin was detected in 15 of 21 sites. Data from years two and three were analyzed by principal components analysis and mixed effects model. Results indicated that coastal nutrient loading (nitrate, phosphate silicate, ammonium, urea), were statistically significant predictors of the microcystin concentrations in the watersheds with clear evidence for seasonality at some sites. Microcystin was frequently at highest concentration in the autumn; however, at some locations high levels of toxin were measured during spring. Because this toxin has the ability to biomagnify and persist within food webs, elevated levels within the watershed may decrease potential for health and survival of wildlife and humans exposed to freshwater and marine waters. The widespread occurrence of microcystin at low to moderate levels throughout the year and throughout the sampled watersheds demonstrates the potential difficulty for management.

1. Introduction

Harmful algal blooms (HABs) are a global problem in both freshwater and marine ecosystems. The prevalence of HABs and subsequent toxic events may be intensified by a warming climate in tandem with increases in environmental degradation and eutrophication (Zehnder and Gorham, 1960; Welker and Steinburg, 2000; Guo, 2007; Paerl and Huisman, 2008; Davis et al., 2009; Kudela, 2011). Production of the toxin microcystin by the cyanobacterium *Microcystis aeruginosa*, was originally recognized by Ashworth and Mason (1946) in American waters in the 1940s. *M. aeruginosa* blooms are now common in lakes and rivers throughout North America, including California (Chen et al., 1993; Lehman et al., 2005). *M. aeruginosa* bloom formation and consequent toxin generation increases with environmental variables such as: high nutrient supply, elevated light levels, and warm temperatures (Zehnder and Gorham, 1960; Tsuji et al., 1994; Jacoby et al., 2000; Welker and Steinburg, 2000; Paerl and Huisman, 2008; Davis et al., 2009; Paerl and Otten, 2013a, 2013b).

Recently toxins associated with the ostensibly freshwater cyanobacterium *Microcystis aeruginosa* have been detected in the near-shore marine ecosystem of central California, and have been confirmed as a danger to the health of sea otters feeding near ocean outflows of freshwater systems (Miller et al., 2010). *M. aeruginosa* is fairly salt-tolerant and microcystin toxins can be stable and environmentally persistent in both saltwater and freshwater habitats (Robson and Hamilton, 2003; Ross et al., 2006; Tonk et al., 2007; Miller et al., 2010). In addition to direct toxic effects, exposure of aquatic organisms to elevated concentrations of microcystins may negatively affect all levels of the food web (Demott and Moxter, 1991; Malbrouck and Kestemont, 2006; Richardson et al., 2007; Miller et al., 2010).

In 2007, numerous sea otters were found dead in Monterey Bay with signs of liver failure (Miller et al., 2010). Biochemical testing confirmed the presence of microcystin toxin with associated lesions in the livers of 21 otters. Because the occurrence of phytoplankton derived biotoxins are a common phenomenon in Monterey Bay, the otters were evaluated for domoic acid, okadaic acid, nodularin, yessotoxin and anatoxin-A. Otters that were found

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positive for microcystin toxin were negative for all other toxins in the tissues. A few of the microcystin positive otters were also found to have low levels of domoic acid in the urine. However, this is a common finding during necropsy of stranded sea otters from this region, due to domoic acid being broadly dispersed in the sediments of Monterey Bay (Goldberg, 2003; Miller et al., 2010). Freshwater to marine transfer of microcystins was confirmed in areas where sea otters had been recovered, and uptake of microcystins by marine invertebrates and environmental persistence in seawater were demonstrated experimentally (Miller et al., 2010). At this time, potential population-level impacts of these biotoxins on otters and other coastal wildlife remains undetermined. The freshwater to marine transfer of microcystin to the Monterey Bay National Marine Sanctuary waters described by Miller et al. (2010) has the potential to cause major environmental harm. The stability of microcystin allows it to accumulate (van der Oost et al., 2003), and microcystin toxin has been shown to biomagnify and persist in the environment and the food web (Sivonen and Jones, 1999; Dionisio Pires et al., 2004; Kozlowsky-Suzuki et al., 2012; Poste and Ozersky, 2013). Despite the confirmation of microcystin poisoning in marine mammals, the source of these toxins is unclear. Pinto Lake, California was identified as a "hotspot" for toxin production and subsequent transfer to the coastal ocean but this source was not consistent with the location of many of the otters (Miller et al., 2010), which were distributed throughout Monterey Bay, suggesting other, less obvious, sources of toxin to the coastal environment.

We took a wide ranging watershed-based approach to identify the potential pathways leading to microcystin contamination in coastal ecosystems in and around Monterey Bay, CA. Since initial surveys of other potential "hotspots" for toxin production were unsuccessful (Miller et al., 2010) via grab sampling, we deployed Solid Phase Adsorption Toxin Tracking (SPATT) samplers throughout the Monterey Bay area to provide a temporally integrated assessment of potential freshwater sources (Kudela, 2011). Because toxin frequency of occurrence, persistence, and associated environmental drivers may potentially be propelling this freshwater toxin into a sensitive and protected marine sanctuary, our overarching goals were to identify the freshwater sources of microcystin to the Monterey Bay ecosystem, and to identify the underlying environmental drivers influencing toxin production in this area.

2. Materials and Methods

2.1. Initial survey

We surveyed 21 freshwater, estuarine, and marine locations in and around the Monterey Bay area at the land–sea interface (June 2010–July 2011) for microcystin toxin presence and concentration (Fig. 1A). Sites included small and large rivers, estuaries, and nearshore marine locations traversing the six watersheds that surround Monterey Bay (Fig. 1A). Each site was sampled monthly using SPATT (Kudela, 2011). SPATT bags were constructed using 3 g DIAION© HP-20 resin (Sorbent Technologies Inc., Georgia, USA) placed between two 3 inch × 3 inch squares of 100 μM Nitex bolting cloth (Wildlife Supply Company, Product No. 24-C34), and secured in a Caron Westex 2.5 in flex embroidery hoop (Caron International, Ontario, Canada). SPATT was activated by soaking each bag in 100% MeOH, for 48 h, and then rinsed with de-ionized water (Milli-Q), and stored in fresh Milli-Q until deployment (Mackenzie et al., 2004; Lane et al., 2010). When deployed at the beginning of each month, SPATT bags were suspended below the surface of the water, and secured with twine to a stake near the edge of the water. This allowed each bag to be suspended in the water, while being weighed down by the ring so that it remained below the surface. Toxin concentration values are reported as nanogram toxin per gram resin. SPATT toxin concentration levels are not directly comparable to grab sample values (ppb, or μg/L), but previous studies suggest a rough correspondence of 10:1 for SPATT to grab samples (Kudela, 2011), i.e. 10 ng/g SPATT is equivalent to an average concentration of 1 ppb microcystin during SPATT deployment.

2.2. Time-series

In years two and three (August 2011–August 2013) sampling locations were reduced to four major affected watersheds in the Monterey Bay area: the Big Basin watershed, Pajaro River watershed, Salinas River watershed, and the Carmel River

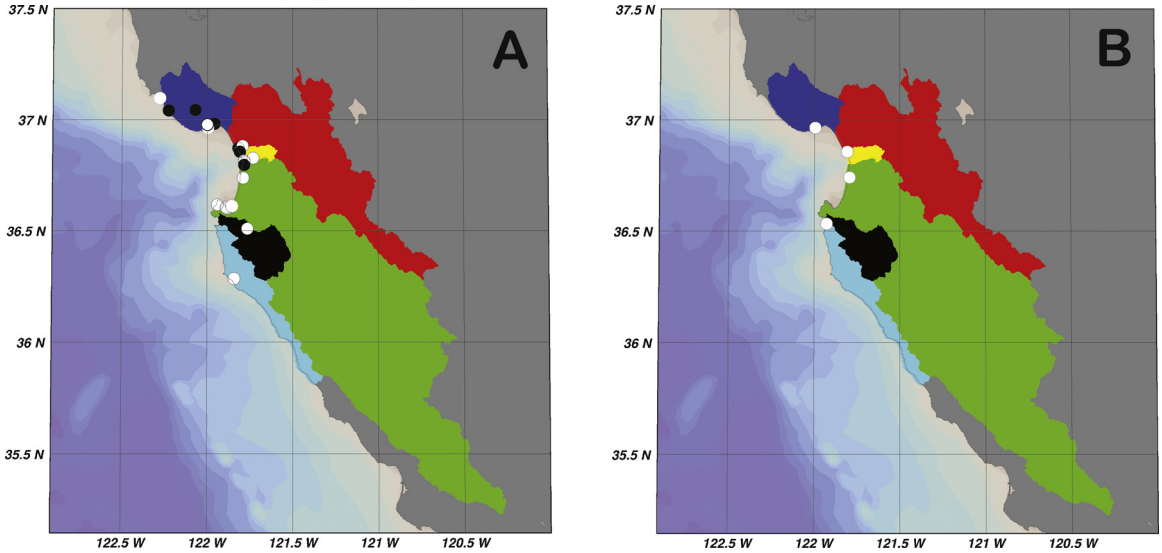

Fig. 1. Map of Monterey Bay, California, USA. (A) Sampling locations in year one (2010–2011) and sampling locations affected by microcystin toxin in year one. White symbols represent sites that were positive for microcystin, black symbols represents sites that were sampled but negative for microcystin toxin. (B) Sampling locations in year two (2011–2013). The watersheds, from north to south, are: Big Basin (dark blue), Pajaro River (red), Bolsa Nueva (yellow), Salinas River (green), Carmel River (black), Santa Lucia (light blue). Ocean bathymetry is indicated with shading. Maps created using Ocean Data View (ODV) and Exelis Visual Information Solutions (ENVI).