Associations between Chlorophyll *a* and various Microcystin-LR Health Advisory Concentrations

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Cyanobacteria harmful algal blooms (cHABs) are associated with a wide range of adverse health effects that stem mostly from the presence of cyanotoxins. To help protect against these impacts, several health advisory levels have been set for some toxins. In particular, one of the more common toxins, microcystin, has several advisory levels set for drinking water and recreational use. However, compared to other water quality measures, field measurements of microcystin are not commonly available due to cost and require advanced understanding to interpret results. Addressing these issues will take time and resources. Thus, there is utility in finding indicators of microcystin that are already widely available, can be estimated quickly and *in situ*, and used as a first defense against high levels of microcystin. In particular, chlorophyll *a* is very commonly measured, can be estimated *in situ*, and has been shown to be positively associated with microcystin. In this paper we use this association to provide estimates of chlorophyll *a* that if exceeded would be indicative of a higher probability of exceeding select health advisory concentrations for microcystin-LR. Using the 2007 National Lakes Assessment and a conditional probability approach that has been used in other water quality settings, we identify chlorophyll *a* concentrations that are more likely than not to be associated with an exceedance of a microcystin health advisory level. We look at the recent US EPA standards for drinking water as well as the World Health Organization levels for drinking water and recreational use. For microcystin concentrations of 0.3, 1, 1.6, and 2 we find chlorophyll *a* concentrations of 21.92, 65.2, 84.24, and 113.14, respectively. When managing for these various microcystin levels exceeding these reported chlorophyll *a* concentrations should be a trigger for further testing and possible management action.

1 Introduction

In the summer of 2014, the city of Toledo, OH was forced to shut down their municipal water supply due in part to an excess of microcystin-LR that resulted from a ongoing cyanobacteria harmful algal bloom (cHAB) in Lake Erie (Rinta-Kanto et al. 2009, Jetoo et al. 2015). Since this event, significant legislation has been passed in the United States and the US Environmental Protection Agency (USEPA) has released suggested microcystin-LR (one of the more common toxins) concentrations that would trigger health advisories (McElhiney and Lawton 2005, Zurawell et al. 2005). MORE ON THE LEVELS. While these levels and associated advisories are likely to help mitigate the impacts from harmful algal

blooms, they are not without complications.

One of these complications is that they rely on available measurements of microcystin-LR. While laboratory testing remains the gold standard for quantifying microcystin-LY concentrations in water samples, several field test kits have been developed. Even though field tests provide a much needed means for rapid assessment, they are infrequently available to lake managers. These kits are moderately expensive (approximately $150-$200 depending on specific kit) with a limited shelf life (typically one year) (James et al. 2011, Aranda-Rodriguez et al. 2015). Additionally, each technique requires nuanced understanding of the detection method (e.g., limit of detection, specific microcystin variants being measured, and sampling protocol). Fortunately, microcystin-LR has been shown to be associated with several other, more commonly measured and understood components of water quality.

Chlorophyll *a* is a very commonly measured components of water quality that is also known to be associated with Microsystin-LR concentrations (Lee et al. 2000, Paerl and Otten (2013)). Additionally there are many rapid measurements for assessing chlorophyll *a* levels *in situ*. For instance, there are small or hand held flourometers that provide reliable measurements [REFS]. Given these facts, it might be possible to identify chlorophyll *a* concentrations that would be associated with the various Microcystin-LR health advisory levels. Identifying these associations would provide another reliable tool for water resource managers to use to help manage the threat to public health posed by cHABs and would be especially useful in the absence of microcystin-LR concentrations. Thus, the goal of this paper is to utlize the National Lakes Assessment data and identify chlorophyll *a* concentrations that are associated with higher probabilities of exceeding several microcystin-LR health advisory concentrations [NLA REF]. So that others may repeat or adjust this analysis, the data, code, and this manuscript are freely available via https://github.com/USAPE/microcystinchla.

2 Methods

2.1 Data

We used the 2007 National Lakes Assessment (NLA) water quality and microcystin-LR concentration data [REF]. These data represent a snapshot of water quality from the summer of 2007 and data on chlorophyll *a* and microcystin-LR concentrations are available for lakes.

2.2 Conditional Probability Analysis

We used a conditional probability analysis (CPA) approach to explore associations between chlorophyll *a* concentrations and World Health Organization (WHO) and U.S. Environmental Protection Agency (U.S. EPA) microcystin-LR health advisory levels (Paul and Munns 2011). Many levels have been suggested (Table 1), but lakes with higher microcystin-LR concentrations in the NLA were rare. Only 1.16 % of lakes sampled had a concentration greater than 10. Thus, for this analysis we focus on the microcystin concentrations that are better represented in the NLA data. These were 0.3, 1, 1.6, and 2 μg/L.

A detailed discussion of CPA is beyond the scope of this paper, but see Paul et al. [-REF] and Hollister et al. [-REF] for details. For this analysis, we used CPA to examine how the conditional probability of exceeding one of the health advisory changes as chlorophyll *a* increases in a lake. The 95% confidence intervals were calculated from 1000 bootstrapped samples. To identify chlorophyll *a* concentrations of concern we used a 50% conditional probability of exceeding each health advisory level and extracted the minimum chlorophyll *a* concentration that was associated with the upper confidence level being 50% or greater. As both microcystin-LR and chlorophyll *a* values were both highely skewed right, a log base 10 transformation was used. Additional details of the specific implementation are available at https://github.com/USEPA/microcystinchla.

3 Results

In the 2007 NLA, microcystin-LR concentrations ranged from 0.05 to 225. Microcystin-LR concentrations of 0.05 μg/L represent the detection limits. Any value greater than that indicates the presence of microcystin-LR. Of those lakes with microcystin, the median concentration was 0.51 and the mean was 0.51. Lastly, of all lakes sampled, 21% of lakes exceeded the U.S. EPA childrens drinking water standard, 8.8% of lakes exceeded the U.S. EPA adult drinking water standard,11.7% of lakes exceeded the WHO drinking water standard,and 7.3% of lakes exceeded the WHO recreational standard. For chlorophyll *a*, the range was 0.07 to 936. All lakes had reported chlorophyll *a* concentrations that exceeded detection limits. The median concentration was 7.79 and the mean was 29.6301946. The associations between chlorophyll *a* and the upper confidence interval with a conditional probability of 50% were 21.92, 65.2, 84.24, and 113.14 for 0.3, 1.0, 1.6 and 2.0 μg/L, respectively (Table 2 & Figure 2).

4 Discussion

The association between Log 10 microcystin-LR and Log 10 chlorophyll *a* show a wedge pattern (Figure 1). This indicates that higher concentrations of microcystin-LR almost always co-occur with higher concentrations of chlorophyll *a* yet the inverse is not true. Higher chlorophyll *a* is not necessarily predictive of higher microcystin-LR concentrations; however, chlorophyll *a* may be predictive of the probability of exceeding a certain concentration.

This is the case as the probability of exceeding each of the four tested health advisory levels increases as a function of chlorophyll *a* concentration (Figure 2). We use this association to identify chlorophyll *a* concentrations that are associated with greater than even odds of exceeding a given health advisory level (Table 2). These represent 29.2%, 11.7%, 8.8%, and 6.3% of sample lakes for the U.S EPA childrens drinking water, the WHO drinking water, the U.S. EPA Adult drinking water, and the WHO recreational standards, respecitvely.

There are numerous possible uses for the chlorophyll *a* and microcystin-LR advisory cut-off values. First, in the absence of microcystin-LR measurements, exceedence of the chlorophyll *a* concentrations

could be a trigger for further actions. Given that there is uncertainity around these chlorophyll *a* cutoffs the best case scenario would be to monitor for chlorophyll and in the event of exceeding a target concentration take water samples and have those samples tested in a lab for microcystin-LR. A second potential use is to identify possible bloom events from historical data. As harmful algal blooms are made up of many species and have various mechanism responsible for adverse impacts (e.g. toxins, hypoxia, odors), there is no single definition of a bloom. For cHABs one approach has been to identify an increase over a baseline concentration of phycocyanin (Miller et al. 2013). This is a useful approach for targeted studies, but phycocyanin is also not always available and measures the predominance of cyanobacterial pigments and not toxins. Using our chlorophyll *a* cutoffs provides a value that is more directly associated with microcystin-LR and can be used to classify lakes, from past surveys, as having bloomed.

These values are conservative: greater than even odds for the upper CI. Most protective.

Not meant as a replacement for testing of microcystin, but provides another useful tool to help understand the probable extent of microcystin occurence.

5 Figures

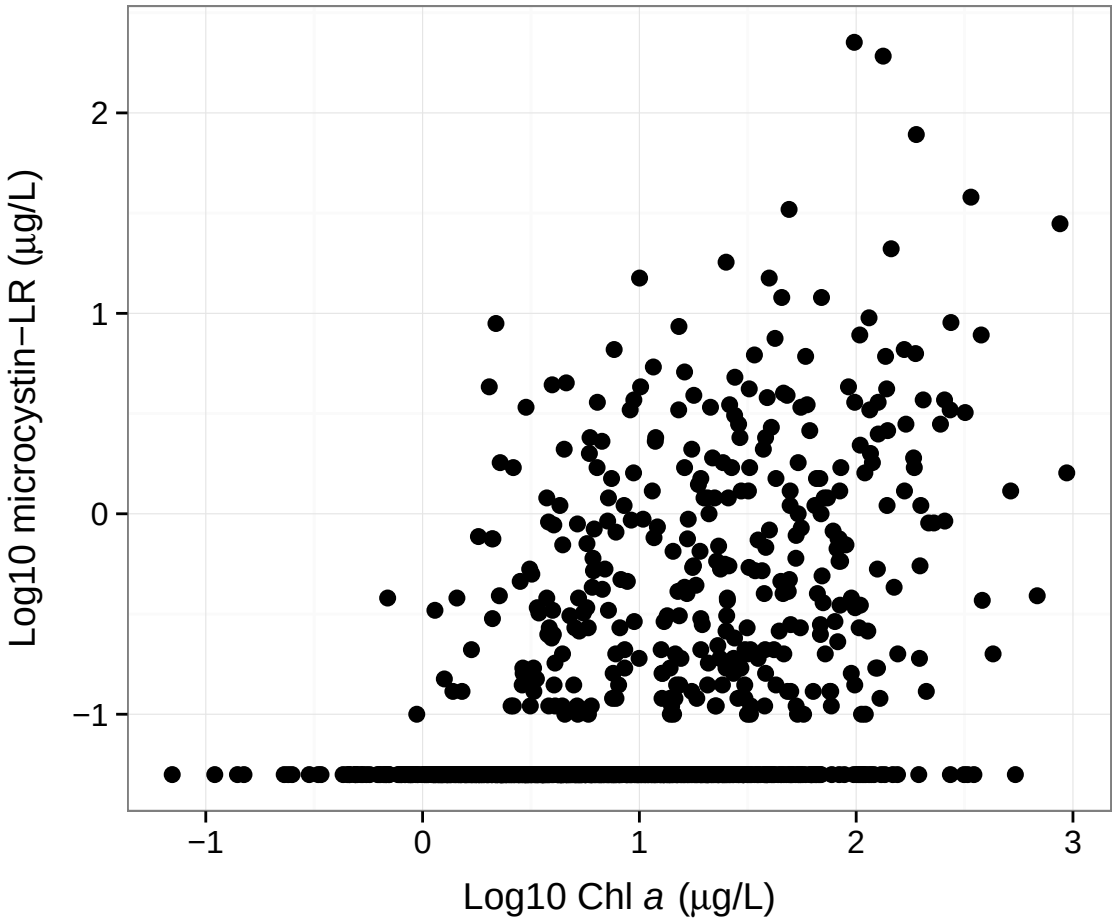

Figure 1: Scatterplot showing association betweeen chlorophyll *a* and microcystin-LR.

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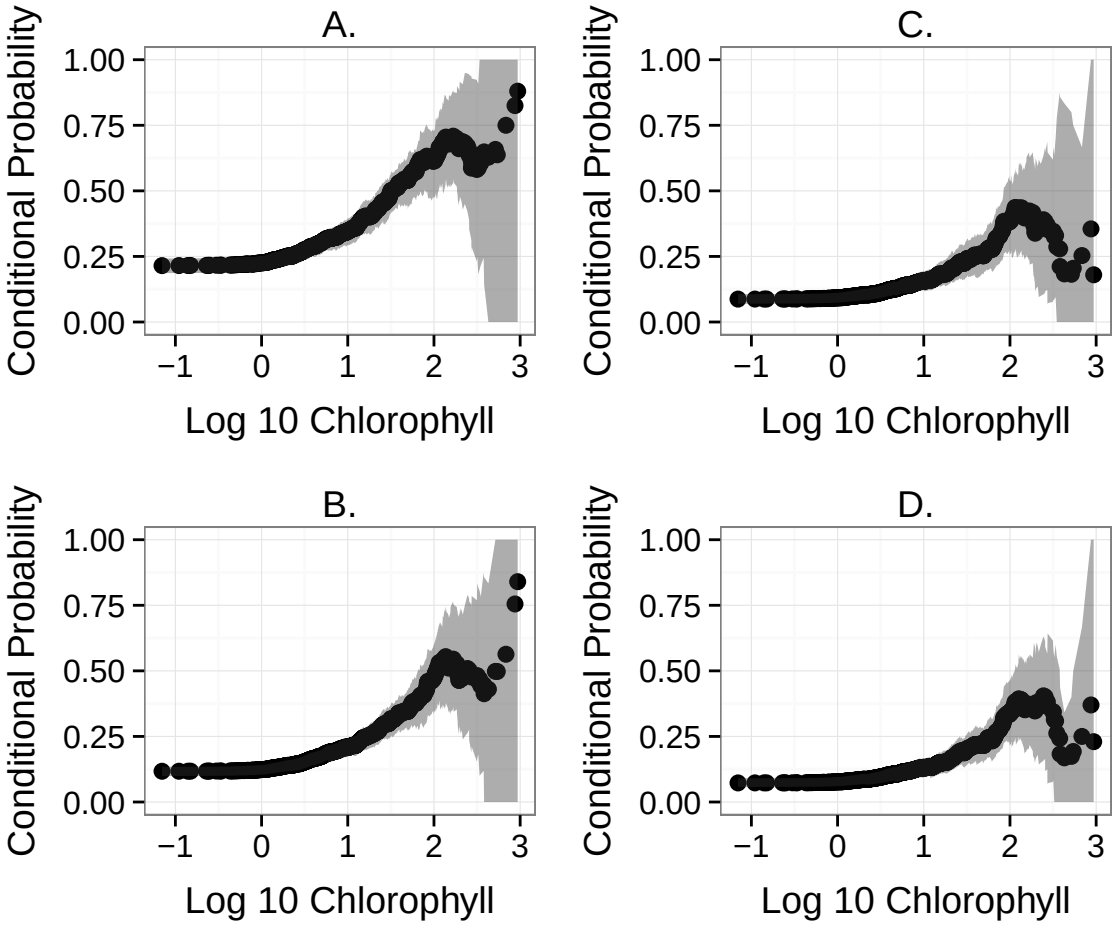

Figure 2: Conditional probability plots showing association between the probability of exceeding various microcystin-LR (MLR) health advisory Levels. A.) Plot for U.S. EPA childrens drinking water advisory (0.3 μg/L). B.) Plot for WHO drinking water advisory (1 μg/L). C.) Plot for U.S. EPA adult drinking water advisory (1.6 μg/L). D.) Plot for WHO recreational advisory (2 μg/L).

6 Tables

Table 1: Various suggested microcystin-LR health advisory concentrations.

Source	Type	Concentration
WHO	Drinking	1 μg/L
U.S. EPA	Drinking	0.3 μg/L
U.S. EPA	Drinking	1.6 μg/L
WHO	Recreational	2-4 μg/L
WHO	Recreational	10-20 μg/L
WHO	Recreational	20-2000 μg/L
WHO	Recreational	>2000 μg/L

Table 2: Chlorophyll *a* concentrations that are associated with a 50% probability of exceeding a microcystin-LR health advisory concentration.

Source	Type	Microcystin	Chlorophyll
U.S. EPA	Drinking	0.3	21.92
WHO	Drinking	1.0	65.20
U.S. EPA	Drinking	1.6	84.24
WHO	Recreational	2.0	113.14

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