1	Does allochthonous dissolved organic matter increase during
2	summer algal bloom conditions in an agricultural reservoir?
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### 30 Abstract

Cyanobacterial harmful algal blooms (cyanoHABs) are increasing in frequency 31 worldwide. CyanoHABs can produce toxins (e.g., microcystin), which can be a contaminant in 32 33 recreational and drinking water reservoirs. Reservoirs have been increasing worldwide, highlighting the importance of understanding their biogeochemical processes. Dissolved organic 34 matter (DOM) is a reactive and readily available source of nitrogen (N) and carbon (C) for 35 36 microbes in aquatic systems, however, the relationships between DOM and cyanoHABs remain 37 relatively unexplored in agricultural reservoirs. Our primary objective is to determine if an increase in allochthonous DOM leads to an increase in autochthonous DOM during a summer 38 39 cyanobacterial bloom event in a warm monomictic agricultural reservoir. Water samples were collected two to three times per week from June 21st until October 5th, 2018 and analyzed for 40 algal biomass and community composition, DOM quality and quantity. A variety of spectral 41 parameters were used to determine DOM quality. One cyanobacterial bloom event was detected 42 on July 16<sup>th</sup>. Maximum microcystin concentration for the sampling period was 0.68 µgL<sup>-1</sup> which 43 is well under the EPA recommended recreational limit (8  $\mu$ gL<sup>-1</sup>). Dissolved organic carbon 44 (DOC) concentrations were positively correlated with high amounts of terrestrial DOM. DOC 45 concentrations and a350 also correlated positively with microcystin concentrations. Specific UV 46 47 absorbance at 254nm (SUVA<sub>254</sub>) correlated positively with Chl-a (r=0.37, p=0.033). Our findings indicate that high DOM quantity has a significant relationship to microcystin 48 49 concentration, which has negative implications for recreation and drinking water quality.

#### 50 Introduction

51 Over the past several decades, cyanobacterial harmful algal blooms (cyanoHABs) have 52 been increasing in frequency worldwide (Huisman et al. 2018). Reservoirs are a primary 53 drinking water and recreation source which can be contaminated by cyanobacteria and lead to the 54 deaths of fish, birds, and even mammals (Chen et al. 2016). As such, it is important that we fully 55 understand the biogeochemical processes that may lead to the formation of toxin producing 56 cyanoHABs.

Dissolved organic matter (DOM) is a reactive, readily available source of carbon (C) and 57 58 nitrogen (N) for microbes in aquatic systems (Jaffé et al. 2008). Excessive nutrient inputs can lead to eutrophication in aquatic systems (Jones and Bachmann 1975). Previous studies have 59 shown a relationship between nutrients such as phosphorus (P) and N and the formation of algal 60 61 blooms (Jones et al., 2004; Paerl et al. 2011; Xu et al. 2015). Although there is extensive literature about the effects of N and P on algal blooms (Levine and Schindler 1998; Smith et al. 62 2006; Jankowiak et al. 2019,), the impacts of dissolved organic matter (DOM) cycling and its 63 relationship to cyanoHABs and toxin concentrations in reservoirs remains relatively unexplored. 64 65 High concentrations of DOM can lead to serious water quality issues including the formation of 66 algal blooms and fish kills as a result of low oxygen concentrations (Creed et al. 2018). DOM may also be contributing to a shift in phytoplankton communities that favors potentially toxin 67 producing cyanobacteria (Creed et al. 2018), though more research is needed to establish the 68 69 relationship. Current knowledge about DOM and C cycling comes largely from studies in coastal 70 and marine systems (Zhao et al. 2009, Osburn and Stedmon 2011, Dixon et al. 2014). Those 71 conducted in freshwater have focused on natural systems such as large rivers and natural lakes 72 (Green and Blough 1994, Cole et al. 2007). It is important to understand inland reservoir

74 (Downing et al. 2006) and have been increasing in number globally (Zarfl et al., 2014).

biogeochemistry and C cycling, as reservoirs contribute significantly to the global C cycle

Small reservoirs have been identified as important sites for C burial (Cole et al. 2007) and 75 efflux (Jones et al. 2016, Pittman et al. 2013); however, DOM cycling has not been thoroughly 76 77 investigated in small agricultural reservoirs in regards to cyanotoxin concentrations. The water 78 quality implications of DOM have been studied in a small subtropical reservoir (Liu et al. 2014); however, possible links with algal blooms, and more specifically with algal toxins, have not been 79 thoroughly explored in small, agricultural reservoirs. Small farm reservoirs make up a significant 80 81 portion of freshwater water bodies in the United States (Downing et al. 2006). Agricultural reservoirs are particularly vulnerable to eutrophication and cyanobacterial blooms (Downing et 82 al. 1999, Wang et al. 2005). The state of Missouri, USA alone has over 190,000 reported small 83 farm ponds (Smith et al. 2002). Missouri waterbodies are primarily man-made reservoirs and 84 63% of Missouri land use is classified as agricultural (Jones and Knowlton, 1993) which 85 highlights the importance of understanding the biogeochemistry of these systems. 86 Previous research has established a positive relationship between high amounts of 87 precipitation events and frequent bloom formation. This is largely due to the influx of nutrients 88

(N and P) into water bodies during a rain event (Michalak et al., 2013). There is also a positive
relationship between high amounts of terrestrial DOM and high amounts of precipitation Dixon
et al., 2014). This research highlights the importance of understanding how rainfall may be
affecting DOM influx into reservoirs.

The optical properties of DOM have been found to be useful in identifying DOM quality (Helms et al., 2008). Our study uses a range of spectrophotometric parameters to determine the source and reactivity of DOM in an agricultural reservoir. Our primary objective is to determine

96 if an increase in allochthonous DOM leads to an increase in autochthonous DOM during a
97 summer cyanobacterial bloom event in a warm monomictic agricultural reservoir. Therefore, we
98 also examine precipitation patterns during the sampling period to determine if changes in DOM
99 are also impacted by precipitation in small agricultural systems.

#### 100 Methodology

#### 101 *Study Site*

An observational study was conducted on Dairy Farm Lake #1, a reservoir in Boone 102 103 County, Missouri, USA (38°99'38"N, 92°48'90"S). Dairy Farm Lake is located on the University of Missouri Experimental Foremost Dairy Farm and is in an agricultural watershed co-managed 104 by the University of Missouri and the Missouri Department of Conservation (MDC). MDC 105 106 manages the fish populations and the lake is open to the public for recreational fishing. Dairy Farm Lake has a surface area of 56,160 m<sup>2</sup> (~15 acres) and a total water volume of 123,920 m<sup>3</sup>. 107 The 639,997 m<sup>2</sup> watershed is 62.94% crop land and 31.85% pasture. The mean depth for Dairy 108 Farm Lake is 2.21 m with a maximum of 4.62 m. All water samples were collected in front of the 109 earthen dam at a depth of 4.3 m. 110

Dairy Farm Lake has been monitored annually by the University of Missouri Limnology
Laboratory as part of the Statewide Lake Assessment Program since 2006, excluding 2015.
Annual monitoring includes analysis of Total Phosphorus (TP), Total Nitrogen (TN), Total
Suspended Solids (TSS), and Chlorophyll-*a* (Chl-*a*) concentrations (Table 1; Eaton et al. 1995).
TP and TN are measured using a digestion and spectrophotometric method (APHA 4500-P E;
Crumpton et al. 1992). Dairy Farm lake is hypereutrophic, based on nutrient criteria of Chl-*a* >40

117	$\mu$ gL <sup>-1</sup> , TP>100 $\mu$ g L <sup>-1</sup> , and TN>1200 mg L <sup>-1</sup> (Jones et al 1993). The average historical Chl- <i>a</i>
118	concentration for Dairy Farm Lake from 2006-2017 is 106.6 µgL <sup>-1</sup> (9.2–772.6 µgL <sup>-1</sup> ; Table 1).

119 Sampling

Samples were collected three times per week from June 21<sup>st</sup> until October 5<sup>th</sup>, 2018. 120 Temperature profiles were measured each sampling day using a YSI EXO 3 temperature probe. 121 122 Profiles were examined in the field to determine the depth of the thermocline. Mixing depth was 123 later calculated using the Lake Analyzer package in R (Winslow et al., 2018); the lake was stratified for the duration of the sampling season. Photosynthetically Active Radiation (PAR) 124 125 was measured using a Li-Cor LI-1500 cosine sensor in guarter meter increments at the water collection site. The light attenuation coefficient (K<sub>d</sub>) was later calculated as described in Kirk 126 (1994). Secchi disk depth and water level changes were also measured each sampling day. A 127 meter stick was placed in the water next to the dam and changes were monitored each sampling 128 129 day. Precipitation data was collected from the Sanborn Field Weather Station located in 130 Columbia, MO, USA.

Samples for analysis of DOM, DOC, and Chl-*a* were collected from both the epilimnion 131 and hypolimnion in 2L polycarbonate bottles. Bottles were previously acid washed and triple 132 133 rinsed with lake water at the sample site before sample collection. Epilimnetic samples were collected using an integrated sampler from the surface to 0.5 m depth. Discrete hypolimnetic 134 samples were taken one meter off the bottom of the reservoir ( $\sim 3$  m from surface) using a Van 135 Dorn sampler. Whole water samples were stored away from light and taken back to the lab for 136 processing on the same day. Water samples to be used for cyanotoxin analysis were collected in 137 polyethylene terephthalate glycol (PETG) bottles to prevent contamination (Kamp et al. 2016). 138 Chlorophyll-a, phytoplankton community composition and biovolumes, and cyanotoxin analyses 139

140	Three freeze-thaw cycles were conducted on the toxin samples. Algal toxin samples were
141	filtered through 0.45 $\mu$ m filters and concentrations were then analyzed using Abraxis <sup>®</sup> ELISA
142	kits with a detection limit of 0.15 $\mu$ gL <sup>-1</sup> and an ELISA Microplate Reader (Carmichael and An,
143	1999). Phytoplankton samples were collected from the epilimnion and preserved with Lugols
144	solution. Chlorophyll-a (Chl-a) concentrations were measured as a proxy for algal biomass. The
145	seasonal mean for Dairy Farm Lake is based on annual samples collected four times per summer
146	from 2006 to 2018 as part of the Statewide Lake Assessment program. Whole water samples
147	were filtered through 0.7 $\mu$ m GF/F filters. Chl- <i>a</i> concentration was determined via extraction
148	with ethanol and fluorometry using a Turner Designs TD-700 Fluorometer and was corrected for
149	pheophytin (Phe-a; Knowlton and Jones 1995).
150	Dissolved organic carbon
151	Whole-water samples from both the epilimnion and hypolimnion were filtered through
152	pre-combusted 0.7 $\mu$ m GF/F filters. The filtrate was used for DOM analysis and absorbance
153	spectroscopy. To determine DOM quantity, we measured dissolved organic carbon concentration
154	(DOC). Prior to analysis, water samples were acidified ( $pH < 3$ ) with 1 M H <sub>2</sub> SO <sub>4</sub> to convert
155	inorganic carbon to CO <sub>2</sub> gas. DOC was measured using a high temperature combustion method
156	(APHA 5310 B) on a Shimadzu TOC-V <sub>CPH</sub> ; detection limit 0.2 mgL <sup>-1</sup> . Samples were air sparged
157	for 7.5 minutes to remove the inorganic carbon. Each sample was measured in two pre-
158	combusted vials, and each of the two vials were measured twice (quadruplicate). Reported DOC
159	concentrations are the average of these four measurements. If the coefficient of variance (CV) of
160	the four measurements was greater than 5, the sample was re-analyzed.

*DOM absorbance spectra* 

162 An indicator of DOM quantity ( $a_{350}$ ) was also determined using UV absorbance 163 spectroscopy on an Agilent Cary 60 UV-Vis spectrophotometer. Each sample was scanned from 164 200 to 800 nm in a 1 cm quartz cuvette. All samples were blank corrected by subtracting the 165 absorbance of UltraPure DI water. Absorption was converted to Napierian absorption coefficient 166 with the equation  $a_{\lambda} = 2.303 A_{\lambda} L^{-1}$  (Osburn and Stedmon, 2011), where a is the absorption 167 coefficient, A is measured absorbance at wavelength  $\lambda$ , and L is the pathlength of the cuvette in 168 meters.

169 DOM quality (i.e., source and reactivity) was also determined using UV absorbance spectroscopy. Specific UV Absorbance (SUVA), normalized for DOC concentration, was 170 calculated at 254nm (a254/[DOC]). SUVA254 provides an indication of molecular weight and 171 aromaticity (Weishaar et al. 2003). Higher SUVA254 values are associated with aromatic and 172 173 allochthonous terrestrially derived DOM (Dixon et al. 2014). The spectral slope ratio was used to characterize both molecular weight and DOM source. Slope ratio  $(S_R)$  was calculated as the ratio 174 of the slopes from wavelengths 275–295 to 350–400 nm (S<sub>275-295</sub>/S<sub>350-400</sub> where S is the slope of 175 176 the absorbance fitted to a single exponential decay function via non-linear regression; Helms et al. 2008).  $S_R$  values greater than one are indicative of autochthonous organic matter with a low 177 molecular weight, while  $S_R$  values less than one indicate allochthonous organic matter with a 178 high molecular weight (Helms et al. 2008). A definition of all measured parameters can be found 179 in Table 2. 180

181 Statistics and Data Analysis

Prior to conducting parametric statistics, the data were confirmed to be normal using a Shapiro-Wilk Test (p>0.05; Base R). All parameters were analyzed for differences between the epilimnion and hypolimnion using a one-way analysis of variance test (ANOVA; multcomp)

185 with the data aggregated into weekly groups. ANOVA was also used to determine differences in

186 each parameter between weeks. Correlation coefficients were calculated using the Pearson

187 method (Hmisc). Correlations were determined to be significant at p < 0.05.

188 Results

## 189 *Limnological variables and precipitation*

The reservoir was stratified for the duration of the sampling period (June 21st to October 5<sup>th</sup>) with an average mixing depth of 2.21 m (range 1.0–4.2). Mean Secchi disk depth for the sampling period was 0.4 m (range 0.3–0.7). The water level did not change during the sampling period as it was a relatively dry season with two significant precipitation events that preceded the detected algal blooms. There was 8.4 mm of rainfall two days before the first bloom occurred on July 16<sup>th</sup>. Similarly, there was 11.9 mm of rainfall four days before the second bloom on September 12<sup>th</sup>.

197 There were significant differences between the epilimnion and hypolimnion for all 198 measured parameters excluding microcystin. The mean Chl-*a* for the epilimnion during the 199 sampling season was 87.0  $\mu$ g Chl-*a* L<sup>-1</sup> (Table 3). Mean dissolved organic carbon (DOC) 200 concentration in the epilimnion was 9.7 mg C L<sup>-1</sup> with a maximum of 10.9 mg C L<sup>-1</sup> and a 201 minimum of 8.8 mg C L<sup>-1</sup>. DOC concentration in the hypolimnion was significantly lower than 202 that of the epilimnion (Table 4) with a mean 9.4 mg C L<sup>-1</sup>, a maximum of 10.9 mg C L<sup>-1</sup> and a 203 minimum was 8.4 mg C L<sup>-1</sup>.

# 204 Cyanobacterial bloom detection

We define a bloom as any deviation from established seasonal Chl-*a* means for the system (Carstensen and Henriksen 2007). The seasonal Chl-*a* mean for Dairy Farm Lake was

106.6 µg Chl-a L<sup>-1</sup> (Table 1). We captured two bloom events during our sampling period which 207 had significantly higher concentrations of Chl-a than the seasonal mean (Figure 1). The first 208 occurred on July 16<sup>th</sup>, with a peak Chl-a value of 162.5 µg Chl-a L<sup>-1</sup>. This bloom was dominated 209 by cyanobacteria (counts; Figure 2) and had a peak microcystin concentration of 0.6  $\mu$ g MC L<sup>-1</sup>. 210 A second bloom event occurred on September 12<sup>th</sup> with a peak Chl-a value of 135.6 µg Chl-a L<sup>-</sup> 211 <sup>1</sup>. This bloom had a microcystin concentrations half that of the first bloom (0.3)  $\mu$ g MC L<sup>-1</sup> 212 (Figure 3, A). Unlike the first bloom event, the second bloom (September 12<sup>th</sup>) was not 213 dominated by cyanobacteria (counts; Figure 2). Microcystin concentrations in the hypolimnion 214 were not significantly different than in the epilimnion, however, the mean for the sampling 215 period was 0.4  $\mu$ g MC L<sup>-1</sup> (0.15  $\mu$ g MC L<sup>-1</sup> to 0.78  $\mu$ g MC L<sup>-1</sup>). 216

# 217 Algal community composition

Preliminary data from phytoplankton counts show that the initial bloom (July 16, 2019) was *Dolichospermum* (formerly known as *Anabaena*.). After this bloom collapsed, there was a second bloom of *Raphidiopsis* (formerly known as *Cylindrospermposis*). It is interesting that these genera were in such high abundance in the reservoir despite the microcystin concentration never being below the detection limit (0.15  $\mu$ g MC L<sup>-1</sup>) in any of our samples. It is supprising that microcystin producing species were not the highest in abundance. Further study should include toxins produced by these genera of algae.

225 Relationship between DOM, Chl-a, and microcystin concentrations

There were significant correlations between the measured DOM parameters and Chl-*a* concentrations. There was no relationship between DOC and Chl-*a*; however, DOM quality assessed by a<sub>350</sub> and SUVA<sub>254</sub> were positively correlated with Chl-*a* (Figure 4). The mean

microcystin concentration in the epilimnion was  $0.3\mu$ g L<sup>-1</sup> (0.15  $\mu$ g MC L<sup>-1</sup> to 0.68  $\mu$ g MC L<sup>-1</sup>; Table 3).

There were significant correlations between DOM quantity and quality and microcystin 231 concentrations. In the epilimnion, DOC correlated positively with microcystin concentrations 232 233 (Figure 5). A significant correlation between these two parameters was also found in the hypolimnion, though the correlation in the hypolimnion was stronger (r=0.63, p<0.0005) than in 234 the epilimnion. Significant positive correlations were also found between a<sub>350</sub> and microcystin; 235 however, it was stronger in the hypolimnion (r=0.49, p<0.003) than in the epilimnion (r=0.34, 236 p=0.047). There was no relationship between SUVA<sub>254</sub> and microcystin in the epilimnion; 237 however, there was a significant positive correlation between the two in the hypolimnion 238 (r=0.35, p=0.040). There were also significant correlations between S<sub>R</sub> and  $a_{350}$  (r=0.65, 239 p < 0.0005), and S<sub>R</sub> and SUVA<sub>254</sub> (r=0.51, p=0.002). S<sub>R</sub> was greater than one for the duration of 240 241 the sampling period indicating high amounts of algal DOM consistently throughout the summer.

242  $S_R$  did not significantly change during the sampling period.

## 243 **Discussion**

The goal of this project was to determine how DOM quantity and quality changes summer algal bloom in an agricultural reservoir. While we saw significant decreases in allochthonous DOM during bloom conditions, there were no significant increases in autochthonous DOM during the bloom event.  $S_R$ , the index used for autochthonous DOM did not significantly change during the bloom events; however, values were greater than 1 for the duration of the sampling period, indicating consistently high amounts of autochthonous DOM (Dixon et al. 2014). 252 High a350 and SUVA<sub>254</sub> values for the duration of the study indicate that this reservoir 253 contains high amounts of terrestrial and aromatic DOM. SUVA254 was significantly lower in the 254 hypolimnion during the cyanobacterial bloom than much of the sampling period (Figure 3B). Phytoplankton degradation is known to be a major source of DOM during algal blooms and 255 256 terrestrially derived DOM has more influence on DOM composition during non-bloom conditions (Zhao et al. 2009). This seems to be the case in our data as well; however, the 257 258 significant decrease in SUVA254 during the bloom occurred only in the hypolimnion. There was 259 also a significant increase in  $S_R$  in the hypolimnion, which may indicate phytoplankton degradation and accumulation in bottom waters. We would also expect to see a decrease in 260 261 SUVA<sub>254</sub> in the epilimnion as well as the hypolimnion, since the bloom is occurring in the epilimnion. It is not clear what would cause such a sharp decrease in SUVA<sub>254</sub> only in the 262 hypolimnion while there was no significant change in the epilimnion during the bloom. 263 264 Significant positive relationships were observed between DOC concentrations, Chl-a, and microcystin. This suggests that there is a relationship between the amount of DOM in an aquatic 265 system and algal abundance. This is supported by previous research that has shown DOM to be a 266 source of nitrogen and carbon for algae (Jaffé et al. 2008). However, research to support a 267 relationship between DOM quantity and microcystin concentration is lacking. 268 269 There was a decrease in DOC from the beginning to the end of the sampling period in 270 both the epilimnion and the hypolimnion. It is possible that this occurred because the algae were

taking up C. In a mesocosm study, a decrease in DOC was documented during an algal bloom.

The authors concluded that it was likely because algae were using the DOC which is likely what

273 happened in this study as well. It is also possible that C assimilation by phytoplankton may have

played a role in sustaining the cyanobacterial bloom (Bai et al. 2017; Morales-Williams et al. 274 2017). At the beginning of the bloom, we saw an increase of allochthonous DOM. As the first 275 bloom progressed, these values decreased, indicating that the algae were using this as a source of 276 nutrients. As the bloom subsided, we saw allochthonous DOM increase again in both the 277 epilimnion and hypolimnion. This suggests a sustained input of allochthonous DOM. This may 278 be the result of runoff from precipitation events as such events were recorded several days before 279 each bloom. Research from under ice algal blooms also supports a relationship between DOM 280 quantity and cyanobacterial biomass (Roiha et al. 2016). It is possible that in this system as well 281 282 that there is a positive relationship between DOM quantity and algal biomass.

# 283 Does DOM quality and quantity correlate with toxin concentration?

We found a significant positive relationship between DOM quantity and microcystin 284 285 concentration. To our knowledge, no other studies have looked for a relationship between DOM and toxin concentrations. The relationship observed between DOM quantity and cyanobacterial 286 287 biovolume suggests that there is an interesting dynamic between DOM and algal community structure. DOM has implications for microcystin concentration during bloom events as well. 288 Microcystin concentrations during first the bloom event exceeded 0.3 µgL<sup>-1</sup>, the EPA 10-day 289 290 drinking water health advisory limit for young children (U.S. EPA 2015), but were well under 291 8.0 µgL<sup>-1</sup>, the EPA recommended swimming advisory limit (U.S. EPA 2019). While our measurements come from raw water, this does highlight concern for the relationships between 292 DOM and toxin concentrations. We did not find any indication of a relationship between DOM 293 quality and toxin concentration. While we tested for relationships between all previously 294 mentioned DOM quality parameters and microcystin, none of them were significant. 295

It is notable that there was no significant difference in microcystin concentrations between the epilimnion and hypolimnion. Since blooms occur in the epilimnion in shallow systems such as this one, it is interesting that microcystin in the hypolimnion were never below the detection limit. This may indicate that microcystin is accumulating in the bottom waters as the bloom crashes or that it is being released from sediments (Zastepa et al. 2015).

#### 301 Conclusion

The results of this study show that there is a relationship between DOM quantity and quality, cyanobacterial bloom formation, and toxin concentration. However, it begs the question: are changes in DOM facilitating cyanobacteria bloom formation and toxin concentrations <u>or</u> did the bloom itself drive the changes in DOM? Unfortunately, we are unable to parse out this distinction with our data. To do this would likely require mesocosm experiments with additions of known quantities and known types of DOM (Rochelle-Newall et al. 1999).

308 Our results highlight the importance of understanding the relationships between DOM, cyanobacterial blooms, and toxin concentrations. There remains much to learn about DOM 309 cycling and its relationship with toxin concentration, particularly in man-made systems. Harmful 310 algal blooms and reservoirs are both increasing worldwide; however, to our knowledge no 311 studies resolving the relationships between DOM and cyanotoxin concentration in reservoirs 312 313 have been published. As cyanobacterial blooms and reservoirs continue to increase, the 314 importance of understanding what factors cause increases in algal biomass and toxin 315 concentration will become essential to finding potential solutions. Reservoirs are increasing worldwide and are an important source of freshwater for much of the population. As such, it is 316 317 important that we fully understand the implications of DOM for cyanoHABs and algal toxicity.

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# **Tables and Figures**

455 Table 1. Characterization table of Dairy Farm Lake #1 from 2006 to 2018 for Total Phosphorous (TP),

456 Total Nitrogen (TN), Chlorophyll-*a* (Chl-*a*), Total Suspended Solids (TSS), and Secchi disk depth

457 (Secchi Transparency).

	TP	TN	Chla	TSS	
Year	$(\mu g L^{-1})$	$(\mu g L^{-1})$	$(\mu g L^{-1})$	$(mg L^{-1})$	Secchi depth (m)
2006	118	2137	69.9	3.7	0.5
2007	105	1645	70.1	4.5	0.6
2008	249	1928	100.4	6.1	0.4
2009	191	2576	108.2	5.8	0.4
2010	218	2781	100.4	3.9	0.4
2011	291	2768	83.8	7.7	0.3
2012	127	1589	54.2	4.3	0.6
2013	148	1544	56.8	6.1	0.6
2014	100	1629	73.3	2.2	0.7
2016	103	1238	55.8	3.6	0.6
2017	95	1463	51.4	1.3	0.6
2018	101	1580	44.7	13.3	0.4

	Parameter	Units	Definition
	Chl-a	μg L <sup>-1</sup>	Chlorophyll-a is used as an indicator of algal biomass.
	Microcystin	$\mu g \; L^{\text{-}1}$	Hepatotoxin released by cyanobacteria and contained within their cells.
	DOC	Mg L <sup>-1</sup>	Dissolved organic carbon. Used as a measurement of DOM quantity.
	a <sub>350</sub>	m <sup>-1</sup>	Napierian absorbance coefficient at 350 nm. a350 is an indicator of terrestrially derived dissolved organic matter.
	SUVA <sub>254</sub>	Lmg <sup>-</sup> <sup>1</sup> Cm <sup>-1</sup>	Specific UV absorbance (SUVA) at 254nm. SUVA is calculated as the Napierian absorption coefficient at 254nm divided by DOC concentration. High SUVA <sub>254</sub> indicates high molecular weight and high aromaticity.
	S <sub>R</sub>	unitless	Slope Ratio. $S_R$ values lower than one are indicative of allochthonous organic matter with a high molecular weight. $S_R$ values greater than one are indicative of autochthonous organic material with high molecular weight.
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Table 2. Abbreviations, units, and definition of each parameter measured or calculated.

Table 3. Summary table of parameters from 2018 sampling season (June 21-October 5) of Dairy Farm Lake #1 including mean, minimum, and maximum values from the epilimnion and hypolimnion. 

492	Definitions of	of each	parameter	and unit	s can	be :	found	in	Table	e 2.
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		Epilimnion			Hypolimnion	
	Mean	Minimum	Maximum	Mean	Minimum	Maximum
DOC	9.7	8.7	10.9	9.4	8.4	10.9
Chl-a	87.0	40.6	162.5	142.9	25.8	384.2
a <sub>254</sub>	39.0	34.9	42.9	48.3	35.1	63.2
SUVA <sub>254</sub>	4.0	3.8	4.4	5.1	3.9	6.7
$S_R$	23.1	4.7	168.5	12.0	3.1	32.2
Microcystin	0.3	0.2	0.7	0.4	0.2	0.8

511 Table 4. One-way ANOVA results for parameters grouped by week measured both in the epilimnion and 512 hypolimnion. All parameters had significant changes (p<0.05) during the sampling period except for a<sub>350</sub>

513 in the epilimnion. A definition of each parameter can be found in Table 2.

	Epilimnion		Hypolimnion	
Parameter	<b>F</b> <sub>(df1, df2)</sub>	р	F <sub>(df1, df2)</sub>	р
Chl-a	3.3(15,18)	0.0083	-	-
Microcystin	5.24(15, 18)	0.0006	4.5(15, 17)	0.002
DOC	8.4(15, 19)	< 0.0005	3.6(15, 18)	0.0057
a350	2.1(15, 19)	0.0657	7.6(15, 18)	< 0.000
SUVA254	5.4(15, 19)	< 0.0005	8.6(15, 18)	< 0.000
SR	3.3(15, 17)	0.0101	2.8(15, 16)	0.0253

535	Table 5: Correlation matrix for DOM	quantity and quality	parameters and their relation to the
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536	concentration of microcystin.	Values represent	correlation	coefficients	(r). Bolded	values indicate
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537	correlations that were significant	(p<0.05).	Definitions for all	parameters car	n be found in Tal	ole 2.
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		DOC		<b>a</b> 350		SUVA <sub>254</sub>		$S_R$		Chla	Microcystin
	DOC	Epi 1	Нуро 1	Epi	Нуро	Epi	Нуро	Epi	Нуро	Epi	Epi
	<b>a</b> 350	0.51	-0.27	1	1						
	SUVA <sub>254</sub>	-0.51	0.06	0.31	0.91	1	1				
	$S_R$	-0.12	-0.12	0.65	0.41	0.51	0.18	1	1		
	Chl-a	0.07	-	0.44	-	0.37	-	0.36	-	1	1
	Microcystin	0.5	0.63	0.34	0.49	0.12	0.35	0.04	-0.05	0.6	1
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- Figure 1: Epilimnetic chlorophyll-a concentrations from June 21<sup>st</sup> to October 5<sup>th</sup> divided into
- 557 weekly aggregates. The first Chl-*a* peak (162.47  $\mu$ g L<sup>-1</sup>) occurred on July 16<sup>th</sup>, 2018. The second
- 558 Chl-*a* peak (135.61  $\mu$ g L<sup>-1</sup>) occurred on September 12<sup>th</sup>, 2018. Both values were significantly
- bigher than historical seasonal means indicating that our observational study included two
- 560 distinct algal blooms. The dotted line represents the historical Chl-*a* mean in Dairy Farm Lake
- 561#1. The x-axis indicates the first day of each sampling week. Different letters indicate
- statistically significant differences between each week.
- 563 Figure 2: A: Cyanobacterial biovolume (mg/m<sup>3</sup>) throughout the sampling period. B: Percent
- 564 cyanobacteria during the sampling period. The highlighted portion in mid-July indicates where
- the algal community was dominated by cyanobacteria (>80% cyanobacteria).
- 566 Figure 3: Timeseries of microcystin, DOC concentration, SUVA<sub>254</sub>, a<sub>350</sub>, and S<sub>R</sub> from June 21<sup>st</sup> to
- 567 October 5<sup>th</sup>, 2018 in the epilimnion. A definition of each parameter can be found in Table 2. A:
- 568 Microcystin concentration, B: DOC concentration, C: SUVA<sub>254</sub>, D:  $a_{350}$ , E:  $S_R$ . The highlighted
- 569 portion in mid-July indicates where the algal community was dominated by cyanobacteria. Each
- 570 box represents one week of sampling. The x-axis indicates the first day of each sampling week.
- 571 Different letters indicate statistically significant differences between each week.
- 572 Figure 4: Timeseries of measured parameters from June 21<sup>st</sup> to October 5<sup>th</sup> in the hypolimnion. A
- definition of each parameter can be found in Table 2. A: Microcystin concentration, B: DOC
- 574 concentration, C: SUVA254, D: a350, E: SR. The highlighted portion in mid-July indicates
- 575 where the algal community was dominated by cyanobacteria. Each box represents one week of
- 576 sampling. The x-axis indicates the first day of each sampling week. Different letters indicate
- 577 statistically significant differences between each week.
- 578 Figure 5: Correlations DOC and microcystin. A: DOC and microcystin in the epilimnion,
- 579 r=0.50, p<0.05; B: DOC and microcystin in the hypolimnion, r=0.50, p<0.05.





595 Figure 2

























661 Figure 5



