

Final Report to Lake Erie Protection Fund

For: SG 501-2015

Can household water purification filters remove microcystin from drinking water?

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Abstract

Toxic cyanobacterial blooms are a global threat to human health due to contamination of drinking water. In order to ensure public safety, water treatment plants must have the capability to remove cyanotoxins from water. Recently, however, there have been several instances when microcystin, a very common and potent hepatic cyanotoxin, has been detected in tap water. This research investigated if commercially available pitcher-style water purifiers are able to remove microcystin from water. Microcystin was extracted from 2 naturally occurring blooms in Lake Erie, diluted to initial concentrations ranging from 1 to 5 ppb, and then subjected to 3 different types of purifiers. The 3 purifiers tested had filter cartridges that had different sources of activated carbon and water percolated through the filter at different rates. Results showed that the purifier with the fastest percolation rate (126 seconds/L) and coconut-based activated carbon removed 50% or less of the microcystin, while the purifier with the slowest percolation rate (374 seconds/L) and a blend of activated carbon decreased microcystin to below detectable levels in all experiments. Dissolved organic nitrogen was also measured and removal efficiency followed a similar pattern to microcystin. Thus, the ability of the pitcher-style purifiers to remove microcystin was a function of contact time and source of activated carbon in the filter cartridge. While some purifiers can serve as an additional barrier against microcystin, it is still recommended to switch water sources if local tap water is known to be contaminated with microcystin.

Introduction

Toxin-producing, freshwater cyanobacterial blooms have become a global threat to the safety of drinking water (He et al., 2016; O'neil et al., 2012; Qin et al., 2010). Cyanobacteria have the potential to produce several “cyanotoxins” that negatively impact several organ systems of vertebrates, including humans (Carmichael, 1992). One of the most potent cyanotoxins, microcystin, is commonly produced by several genera of cyanobacteria and was responsible for the 2014 “do not drink” advisory in Toledo, Ohio that left more than 400,000 residents without potable tap water (Bullerjahn et al., 2016). Unfortunately, cyanobacterial blooms are predicted to become more severe and wide-spread with climate change if land use practices are not altered to minimize nutrient (phosphorus and nitrogen) input to surface waters (Michalak et al., 2013; Paerl et al., 2016). Recent improvements to land use and sewage treatment are ongoing in effort to prevent blooms, but in the meantime the ability to remove microcystin from surface water to insure public safety is crucial.

The majority of research conducted regarding removing microcystin from drinking water has occurred at the water treatment plant scale. Common methods include activated carbon (Ho et al., 2011), UV light and hydrogen peroxide oxidation (He et al., 2012), and ozone (Hitzfeld et al., 2000). At the resident scale, Pawlowicz et al., (2006) showed that carbon-based under-the-sink filters that are connected to the faucet will remove more than 99.7% of microcystin spiked into deionized water. However, they also showed that pleated paper and string wound filters allowed more than 90% of microcystin to pass through (Pawlowicz et al., 2006). Thus, the effectiveness of the filters depends on how the filter is created. The ability of point-of-use filters, such as pitcher-style water purifiers, to remove microcystin from water have not been tested.

The objective of this project was to determine if household pitcher-style water purifiers are effective at removing microcystin from water. Microcystin was extracted from 2 natural Lake Erie cyanobacterial blooms (*Microcystis* and *Planktothrix* blooms) which were subjected to the purifiers. This method replicates a more realistic scenario than spiking pure microcystin in deionized water, as water treatment plants draw in lake water that contains natural organic matter (NOM) along with potentially toxic cyanobacteria. It is likely that NOM would also break through the treatment process if microcystin broke through, as evident as taste and odor problems associated with drinking water (Watson et al., 2016), and because NOM competes with microcystin for adsorption sites on activated carbon (Lambert et al., 1996). Initial concentrations of the microcystin in these experiments were between 0.8 and 5.0 ppb, which spans the range of likely microcystin concentrations in Toledo's tap water during the 2014 crisis (Qian et al., 2015). Three different types of purifier filter cartridges were tested in both new and expired conditions. Finally, repeated filtering through the purifiers was tested to determine if microcystin removal could be increased with increased filter contact time. Additionally, dissolved organic nitrogen (DON) was quantified as a proxy for dissolved organic compounds, other cyanotoxins, and taste and odor compounds.

Methods

Microcystin collection and experiment preparation

Lake water containing microcystin-producing cyanobacteria was collected on 24 July, 2015 from Put-in-Bay during a *Microcystis* surface scum and on August 10, 2015 from Sandusky Bay during a *Planktothrix* bloom. Approximately 20 L of water was collected from each bloom and subjected to 4 freeze/thaw cycles to lyse cells and extract microcystin, and concentration was

measured using ELISA (see below). The water was held at -20°C until experimentation. On the day of an experiment, water was thawed, filtered through GFF filters (0.45 µm) to remove cellular debris, and diluted with deionized (DI) water to lower the microcystin concentration to 1 to 5 ppb.

Microcystin congeners present in the bloom-extracted samples were identified and quantified by GreenWater Laboratories (Palatka, Florida, USA) by liquid chromatography with tandem mass spectrometry (LC-MS/MS). Fourteen congeners were analyzed for and method detection limit ranged from 0.01 to 0.05 ppb for each congener.

Water purifiers

Commercially-available pitcher-style water purifiers and corresponding filter cartridges were purchased from a local super market. Three different purifier brands were tested and each brand's had unique filter cartridge components (Table 1). Thus, tests were conducted on the components of the filter cartridge and not necessarily the brands as each brand may manufacture different 'grades' of filter cartridge. All pitchers used in the study held between 2.4 L and 2.6 L of water. Three separate pitcher-style water purifiers of each type were used as replicates (9 total pitchers) and water poured into pint glasses served as a non-purified control.

New filter cartridges were installed according to manufacturer instructions. In order to determine if the filter cartridges would somehow result in a false positive for microcystin, 1 L of DI water was poured into the pitchers and that water was sampled for microcystin after it had percolated through the filter cartridge. All samples in this test were below the detection limit. Additionally, pH and chloride concentration were measured and verified to be within range so as to not adversely affect the microcystin ELISA test (pH between 5 and 11, Cl < 0.10 mg/L). The tests described below were also conducted on expired filter cartridges, which were expired by

pouring tap water through the pitchers until the cartridge was considered to be expired according to manufacturer instructions.

Percolation rates of the purifiers were quantified by timing the length of time elapsed as 1 L of tap water to percolate through each filter. For the remainder of this report, each purifier is identified by the time needed for 1 L to percolate (seconds/L).

Experimental methods

Objectives of this study were designed to determine if the pitcher-style water purifiers (1) can remove microcystin and dissolved organic nitrogen (DON) from water, (2) will leak microcystin after remaining idle for 4 hours (as if filled and placed in a refrigerator for future use), and (3) if microcystin will become unbound from the filter cartridge upon filtering microcystin-free water. In order to determine if the pitchers remove microcystin and DON from water, 1 L of water containing microcystin was poured into each purifier. Water samples were collected both before and immediately after all water percolated through the filter cartridge. Each purifier was subsampled 3 times for microcystin by pipetting 10 mL of water from the pitcher purifier into an amber glass vial (which were averaged to determine the microcystin concentration for that purifier) and one 150 mL sample was collected for DON analysis by pouring water from the purifier into a 250-mL polycarbonate bottle. Microcystin analysis began immediately while the DON samples were stored at -20°C until analysis. To determine if the filter cartridges leaked microcystin back into the water, microcystin samples were also collected 4 hours after initial filtration. Finally, to determine if microcystin became unbound from the filter cartridge the water was discarded and 1 L of DI water (microcystin free water) was poured into the purifier and sampled for microcystin after it percolated through the filter cartridge. These

experiments were conducted with new and expired filter cartridges and with two naturally occurring sources of microcystin in Lake Erie (*Microcystis* and *Planktothrix* blooms).

Percolation rates differed remarkably among the 3 types of purifiers (see results, Table 1); therefore, an experiment was designed to determine if increased filter contact time would increase microcystin and DON removal. In separate experiments using new filter cartridges, 1L of *Microcystis*-microcystin water was poured into each purifier and sampled for microcystin as above. The water was then poured out of the purifier, into a clean glass beaker, and then back into the purifier. This process was repeated 3 times with a microcystin sample collected after each percolation. Water for DON analysis was only sampled after the final purification step. This experiment was conducted twice, once using water with an initial microcystin concentration of 0.96 ppb and then again with initial water with microcystin concentration of 4.8 ppb.

Quantification Analysis

Microcystin was quantified using enzyme-linked immunosorbent assay (ELISA) following Ohio EPA protocol #701.2 with Abraxis kits. All standards and subsamples were analyzed in duplicate. For all ELISA results accepted in this research, the R^2 values between known concentrations standards (0.0 to 5.0 ppb) and measured absorbance were 0.98 or greater, lab reagent blanks (LRB) were all below the reporting limit, and low calibration range check (LCRC, 0.4 ppb) were within acceptable ranges. Microcystin concentration results less than 0.15 ppb were considered below detectable levels. All ELISA tests were conducted by analysts certified by the Ohio EPA.

DON was quantified using Kjeldahl digestions and quantification as ammonia, following standard method EPA 351.2. All DON samples were analyzed in duplicate.

Data analysis

Many of the samples analyzed with ELISA gave microcystin concentrations below detectable concentrations (< 0.15 ppb). However, ELISA will always estimate a concentration value greater than 0.05 ppb, even for lab reagents blanks (DI water) which have zero microcystin. The estimated concentrations were used to calculate treatment averages even when the value was less than the method detection limit (MDL). Analysis of variance (ANOVA) with a post hoc Tukey test was used to test for differences among treatments.

Results

Filter contact times were remarkably different among the 3 types of purifiers as 1 L of tap water needed 125.9 ± 2.41 seconds, 230.9 ± 7.30 seconds, and 374.0 ± 2.41 seconds to pass through the filters. These contact times converted to flow rates gave 0.48 ± 0.009 L/min, 0.26 ± 0.009 L/min, and 0.16 ± 0.001 L/min. For the remainder of this report, each filter type is identified by the contact time of 1 L (126-purifier, 231-purifier, 374-purifier).

Microcystin-RR was the most abundant congener identified from both the *Microcystis* and *Planktothrix* bloom extractions (Table 2). Microcystin-YR and -LR were found in both samples. Low levels of Microcystin-HtyR and [DAsp³]microcystin-LR identified from *Microcystis* and *Planktothrix*, respectively (Table 2). Nine other congeners that were tested for in both samples were below method detection limit.

Figures in the result section display the treatment averages of the estimated microcystin concentration and values less than the MDL, but the true microcystin concentration could range from zero to 0.15 ppb. Hence, it could not be confirmed or denied that the purifiers removed 100% of the microcystin.

Initial microcystin concentration in the *Microcystis*-extracted water was 3.3 ppb (Fig. 1A). Microcystin concentration significantly ($P < 0.001$) decreased following percolation through each purifier, but was detected in the filtered water from 2 of the 3 purifiers (Fig. 1A). The 126-purifier decreased microcystin to 1.88 ± 0.21 ppb and the 231-purifier decreased microcystin to 0.50 ± 0.05 ppb. Microcystin was decreased to non-detectable levels by the 374-purifier. Microcystin concentration in the filtered water did not change 4 hours after percolation, and microcystin was not detected in DI water that was filtered through the purifiers. The experiment was repeated for expired filter cartridges with *Microcystis*-extracted microcystin with an initial concentration of 1.94 ppb (Fig. 1B). Following percolation, water from the 126-purifier was significantly similar to the non-filtered control. The 231-purifier decreased microcystin to 0.25 ± 0.03 ppb and the 374-purifier decreased microcystin to non-detectable levels. Again, the microcystin concentrations did not change after 4 hours and were not detectable following a DI water flush. *Planktothrix*-extracted microcystin had an initial concentration of 2.90 ppb (Fig. 1C). The 126-purifier decreased microcystin to 0.28 ± 0.03 ppb, while the 231- and 374-purifiers decreased microcystin to below detectable levels. Again, the microcystin concentrations did not change after 4 hours and were not detectable following a DI water flush.

Dissolved organic nitrogen (DON) was measured on water that passed through the purifiers (but was not measured following 4 hour and not after a DI flush). In the new filter *Microcystis*-extracted experiment, the initial DON concentration was 252.9 ppb and the 126-, 231-, and 374-purifier significantly ($P < 0.001$) decreased DON to 191.9 ± 6.7 ppb, 144.2 ± 11.9 ppb, and 21.9 ± 2.1 ppb, respectively (Fig. 2A). In the expired *Microcystis*-extracted experiment, the 126-purifier decreased DON to the lowest levels while the water of 374-purifier had significantly similar DON concentration as the non-filtered control (Fig. 2B). Initial DON of the

Planktothrix-extracted experiment was much higher than the *Microcystis*-extracted water at 782.5 ppb (Fig. 2C). DON concentration actually increased following percolation through the 126-purifier, while the 231- and 374-purifier decrease DON to 272.5 ± 12.5 ppb and 18.0 ± 2.2 ppb, respectively (Fig. 2C).

Because percolation rates (i.e. contact times) differed an experiment to equalize contact time was conducted. The quickest percolating purifier (126 seconds/L), was about 3 times as fast as the slowest percolating 374-purifier. Water from the 126-purifier was filtered 3 times in total (refiltered 2 times after initial contact) to increase contact time to a similar contact time as the 374-purifier. The filter with the intermediate contact time of 231 seconds/L was filtered twice. Therefore, this experiment standardized contact time among the 3 purifiers. Initial concentrations for the 2 experiments conducted were 0.89 ppb (Fig. 3A) and 4.70 ppb (Fig. 3B) of *Microcystis*-extracted microcystin. The 374-purifier decreased microcystin to below detectable levels in both the low and high initial microcystin experiment after 1-time percolation (Fig. 3). The 231- and 126-purifier decreased microcystin concentration in a step-wise fashion, but the 231-purifier decreased microcystin more than the 126-purifier. In the high microcystin experiment, the 231-purifier decreased microcystin to 1.00 ± 0.03 ppb after one percolation then to 0.29 ± 0.02 ppb after two percolations, while the 126-purifier decreased microcystin to 2.64 ± 0.01 ppb, 1.60 ± 0.05 ppb, and 1.01 ± 0.02 , respectively, ppb after each percolation step (Fig. 3B).

DON was only determined after the final percolation step for the repeated percolation experiment. There was no significant difference in DON concentration among the purifiers in the low initial concentration experiment ($P = 0.059$; Fig. 4A). Initial DON concentration was 240.4 in the high experiment (Fig. 4B). After 3-time percolation through the 126-purifier, DON was reduced to 115.0 ± 9.60 ppb, while 2-time percolation through the 231-purifier reduced DON to

80.0 ± 1.45 ppb. DON concentration was reduced to 19.0 ± 7.39 ppb after 1-time percolation through the 374-purifier.

Discussion

It has been forecasted that toxic cyanobacterial blooms will increase in magnitude under current climate change scenarios (Michalak et al., 2013; Paerl and Huisman, 2008). Therefore, it is paramount that all possible actions (land use and water treatment actions) are taken to remove cyanobacterial toxins from water to provide safe drinking water. A common question asked of scientists who study cyanobacteria and water treatment plant operators by the public is “Does my water pitcher filter out microcystin?” Results from this study demonstrated that water pitcher-style purifiers can add another layer of defense against microcystin; however, the amount of microcystin removed varied among different purifiers.

The ability of each purifier to remove microcystin and DON was largely a function of percolation rates as the filter with the quickest percolation (lowest contact time) removed the least amount of microcystin and DON whereas the filter with the slowest percolation (greatest contact time) decreased microcystin to below detectable levels in all experiments. The experiment of repeated percolations with high initial microcystin (Fig. 3B) suggested that more microcystin would have been removed by the 126- and 231-purifiers if they had longer contact times. However, after the third time the microcystin-water was poured through the 126-purifier (total contact time of 378 seconds/L) the microcystin concentration was still at 1.0 ppb, which was unlike the one-time percolation of the 374-purifier which decreased microcystin to below detectable levels. This result also indicates that the contents of the filter cartridges also impacted microcystin removal.

Activated carbon is a major component of all three filter cartridges tested and is one of the several methods used by water treatment plants to remove dissolved organics, including microcystin, from drinking water (as reviewed by He et al. 2016). There are several sources of activated carbon (wood, coal, coconut, peat moss) and their efficiency to remove organics varies due to the size of pores created upon activation (“micropores” < 2.0 nm, “mesopores” 2-50 nm, and “macropores” > 50 nm). The small pores are more suited for adsorption of small compounds while larger pores are more suited for the adsorption of high molecular weight compounds. Microcystins are in the 1-3 nm range and more effectively adsorbed by mesopores (Pendleton et al., 2001). Coconut shells, which produce micropores upon activation (Donati et al., 1994; Pendleton et al., 2001), were listed as the main carbon source for the 126-purifier. Thus, the 126-purifier is not well suited to remove microcystin due to the lack of mesopores. Wood-based activated carbon produces both micropores and mesopores and has been shown to have the highest microcystin removal efficiency (Donati et al., 1994; Pendleton et al., 2001). The 231- and 374-purifiers advertise that a “blend” of activated carbon was used; however, the composition of that carbon blend was unknown.

Microcystin concentration did not differ between samples collected immediately after percolation and 4 hours after percolation (Fig. 1). Furthermore, microcystin was not detected in DI water that was percolated through the purifiers after the microcystin-laden water was discarded. These results indicate that microcystin bound to the activated carbon did not become unbound with repeated use. These were true for both new and expired filter cartridges; however, the expired 126-purifiers did not significantly decrease microcystin (Fig. 1B).

Microcystin is a very common toxin produced by many different bloom-forming cyanobacteria genera, but cyanobacteria can produce many other toxins that have harmful

impacts on human health, such as anatoxin, saxitoxin, and cylindrospermopsin (Huisman et al., 2010). However, the results of this study cannot be extrapolated to the other cyanotoxins due to the differing molecular size (anatoxin-a 165 g/mol, saxitoxin 300 g/mol, cylindrospermopsin 415 g/mol, microcystins 900-1050 g/mol (Carmichael, 1992; Ho et al., 2011)) and the efficiency of different activated carbon to remove different size of organic molecules. For example, Ho et al. (2011) showed that the adsorption of cylindrospermopsin and microcystins by coal-based powdered activated carbon differed at shorter contact times and small doses; however, Ho et al. (2011) also showed that with increased contact time and dose that both cyanotoxins were effectively 100% removed from water.

During times when microcystin has been detected in drinking water above advisory limits and a “do not drink” advisory is issued, it is recommended that users switch water sources for consumption. The US EPA current advisory levels for microcystin are based on a 10-day average at concentrations of 0.3 ppb for children and 1.6 ppb for adults. Only 1 of the 3 purifiers tested in this research decreased microcystin to less than 0.3 ppb in all tests (it was also below detectable levels). Furthermore, because the relatively high method detection limit of ELISA (0.15 ppb), it is unknown if the 374-purifier removed all of the microcystin. Therefore, when microcystin is known to be in tap water, it is suggested the consumers switch to bottled water or obtain water from another public water system. However, for consumers who may not trust public drinking water due to undetected microcystin (either below detection limits or in between tests) and instead purchase bottled water, pitcher style water purifiers would be a more-economical and less-wasteful "safety net" option than bottled water. However, purifiers were intentionally not identified by brand/model in this report, users may not be able to directly relate their purifier these results.

The global public health organization NSF International recently issued a new protocol (#477) that will allow manufacturers of point-of-use water purifiers to make claims that their product can decrease microcystin to concentrations less than 0.3 ppb (NSF International, 2016). Results from this study indicate only the 374-purifier would achieve that certification. However, the lower the initial microcystin concentration the greater the chance that any purifier can decrease microcystin to 0.3 ppb. For example, the 126-purifier achieved 0.3 ppb when the initial microcystin concentration was 0.89 ppb (Fig. 3A), but the 126-purifier did not achieve 0.3 ppb when initial microcystin concentration was 1.9 ppb or greater (Figs. 1A, B, C, 3B).

In conclusion, the amount of microcystin removed by point-of-use pitcher style purifiers differed by type of filter cartridge. The purifier that was most effective at removing microcystin had the slowest percolation time and a cartridge not solely based from coconut shell activated carbon, whereas the purifier with the quickest rate of percolation and coconut-based activated carbon removed the least amount of microcystin. Because cyanobacterial blooms will likely persist in the near future, water pitcher purifiers maybe an effective method for consumers to remove microcystin from tap water if there is concern about trace levels of microcystin passing through treatment undetected on non-testing days. Nonetheless, it is still recommended that consumers switch water sources during times when microcystin is known to be present in tap water.

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Changes and hurdles

In summer 2015 the undergraduate students arrived at the lab about one month before funding began and had to leave just as the supplies started to arrive. Therefore an extension was requested and received to allow 2016 students work on the project. In spring 2016, 3 undergraduate students were selected to work in the lab and offered to work on 1 of several research projects, but none of them selected to work on this water pitcher experiment because they wanted to study the ecology of blooms. Despite none of the students wanting to write a report for this project, all 3 students had roles in the project. The students were the ones who extracted the microcystin, poured the microcystin-laden water into the pitchers, collected the samples, timed the percolation rates of the pitchers, and helped with sample analysis.

In the proposal we indicated that an experiment would have been conducted with pure microcystin spiked into deionized water. However, that was not feasible due to Ohio State University codes regarding concentrated pure microcystin in the laboratory. The project would have been significantly delayed in order to be permitted to have pure microcystin in the lab. Thus, the experiments where pure microcystin were omitted and replaced with the repeated filtering experiments (Figs. 3 and 4). Furthermore, deionized water spiked with microcystin does not simulate natural settings because natural organic matter will also be present in the natural water and that organic matter competes with microcystin for binding on the activated carbon.

Dissolved organic nitrogen was added to the sample analysis because we wanted another parameter to measure along with microcystin.

Different congeners of microcystin from the initial bloom sources were identified.

Activities and Timeline

July – August 2015: Purchased supplies required for the study. Collected *Microcystis* and *Planktothrix* bloom samples.

September – October 2015: Conducted the experiments using *Microcystis*-extracted microcystin and analyzed the samples for microcystin and DON (Figs. 1A, 1B, 2A, and 2B).

November 2015- May 2015: Analyze data from the experiments conducted. Found out that the pure microcystin experiment was not feasible and developed plans for summer 2015.

June - August 2016: Undergraduate researchers at the lab. Conduct the remaining experiments. Continued data analysis and began writing the report.

September 2016: Finalize and submit report. Poster developed that will be on display in our Aquatic Visitors Center beginning May 2017. Results from the project were shared at Stone Lab education and outreach events and the results will continued to be shared past the funding timeline of the project.

Deliverables

We learned that the ability of pitcher-style purifiers to remove microcystin depended on filter contact time and the type of activated carbon in the filter cartridge. Quick percolation through the filter (short filter contact time) and coconut-based activated carbon had the lowest efficiency at removing microcystin. The purifier that had slow percolation (high filter contact

time) and a blend of activated carbon decreased microcystin to below detection in all experiments. This information can be shared with the public who are looking for additional protection from microcystin in tap water.

A poster highlighting the results and conclusions from this research will be on display in our Aquatic Visitors Center in 2017, which receives over 25,000 visitors each summer.

A future edition of Ohio Sea Grant's publication "Twinline" will feature the results of this project. That edition will be published and mailed to subscribers in October 2016. That edition will also be available at this link <https://ohioseagrant.osu.edu/products/twinline> as soon as it is finished have a final file.

3 undergraduate research students were helped with this research.

References

- Bullerjahn, G.S., McKay, R.M., Davis, T.W., Baker, D.B., Boyer, G.L., D'Anglada, L.V., Doucette, G.J., Ho, J.C., Irwin, E.G., Kling, C.L., Kudela, R.M., Kurmayer, R., Michalak, A.M., Ortiz, J.D., Otten, T.G., Paerl, H.W., Qin, B., Sohngen, B.L., Stumpf, R.P., Visser, P.M., Wilhelm, S.W., 2016. Global solutions to regional problems: Collecting global expertise to address the problem of harmful cyanobacterial blooms. A Lake Erie case study. *Harmful Algae*, 54, 223–238. doi:10.1016/j.hal.2016.01.003
- Carmichael, W. W., 1992. Cyanobacteria secondary metabolites—the cyanotoxins. *J. Appl. Bacteriol.* 72, 445–459. doi:10.1111/j.1365-2672.1992.tb01858.x
- Donati, C., Drikas, M., Hayes, R., Newcombe, G., 1994. Microcystin-LR adsorption by powdered activated carbon. *Water Res.* 28, 1735–1742. doi:10.1016/0043-1354(94)90245-3
- He, X., Liu, Y.-L., Conklin, A., Westrick, J., Weavers, L.K., Dionysiou, D.D., Lenhart, J.J., Mouser, P.J., Szlag, D., Walker, H.W., 2016. Toxic cyanobacteria and drinking water: Impacts, detection, and treatment. *Harmful Algae*, 54, 174–193. doi:10.1016/j.hal.2016.01.001
- He, X., Pelaez, M., Westrick, J.A., O'Shea, K.E., Hiskia, A., Triantis, T., Kaloudis, T., Stefan, M.I., de la Cruz, A.A., Dionysiou, D.D., 2012. Efficient removal of microcystin-LR by UV-C/H₂O₂ in synthetic and natural water samples. *Water Res.*, 46, 1501–1510. doi:10.1016/j.watres.2011.11.009
- Hitzfeld, B.C., Höger, S.J., Dietrich, D.R., 2000. Cyanobacterial toxins: removal during drinking water treatment, and human risk assessment. *Environ. Health Perspect.* 108, 113–122.
- Ho, L., Lambling, P., Bustamante, H., Duker, P., Newcombe, G., 2011. Application of powdered activated carbon for the adsorption of cylindrospermopsin and microcystin toxins from drinking water supplies. *Water Res.* 45, 2954–2964. doi:10.1016/j.watres.2011.03.014
- Huisman, J., Matthijs, H.C.P., Visser, P.M. (Eds.), 2005. *Harmful Cyanobacteria*. Springer.
- Lambert, T.W., Holmes, C.F.B., Hrudehy, S.E., 1996. Adsorption of microcystin-LR by activated carbon and removal in full scale water treatment. *Water Res.*, 30, 1411-1422.
- Michalak, A.M., Anderson, E.J., Beletsky, D., Boland, S., Bosch, N.S., Bridgeman, T.B., Chaffin, J.D., Cho, K., Confesor, R., Daloğlu, I., DePinto, J.V., Evans, M.A., Fahnenstiel, G.L., He, L., Ho, J.C., Jenkins, L., Johengen, T.H., Kuo, K.C., LaPorte, E., Liu, X., McWilliams, M.R., Moore, M.R., Posselt, D.J., Richards, R.P., Scavia, D., Steiner, A.L., Verhamme, E., Wright, D.M., Zagorski, M.A., 2013. Record-setting algal bloom in Lake Erie caused by agricultural and meteorological trends consistent with expected future conditions. *Proc. Natl. Acad. Sci.* 110, 6448–6452. doi:10.1073/pnas.1216006110

- NSF International, 2016. <http://www.nsf.org/newsroom/nsf-international-certifies-first-water-filters-that-reduce-microcystin-in>. Accessed 15 March 2016.
- O'Neil, J.M., Davis, T.W., Burford, M.A., Gobler, C.J., 2012. The rise of harmful cyanobacteria blooms: the potential roles of eutrophication and climate change. *Harmful Algae* 14, 313–334.
- Paerl, H.W., Gardner, W.S., Havens, K.E., Joyner, A.R., McCarthy, M.J., Newell, S.E., Qin, B., Scott, J.T., 2016. Mitigating cyanobacterial harmful algal blooms in aquatic ecosystems impacted by climate change and anthropogenic nutrients. *Harmful Algae*, 54, 213–222. doi:10.1016/j.hal.2015.09.009
- Paerl, H.W., Huisman, J., 2008. Blooms Like It Hot. *Science* 320, 57–58. doi:10.1126/science.1155398
- Pawlowicz, M.B., Evans, J.E., Johnson, D.R., Brooks, R.G., 2006. A study of the efficacy of various home filtration substrates in the removal of microcystin-LR from drinking water. *J. Water Health* 4, 99–107.
- Pendleton, P., Schumann, R., Wong, S.H., 2001. Microcystin-LR Adsorption by Activated Carbon. *J. Colloid Interface Sci.* 240, 1–8. doi:10.1006/jcis.2001.7616
- Qian, S.S., Chaffin, J.D., DuFour, M.R., Sherman, J.J., Golnick, P.C., Collier, C.D., Nummer, S.A., Margida, M.G., 2015. Quantifying and reducing uncertainty in estimated microcystin concentrations from the ELISA method. *Environ. Sci. Technol.* 49, 14221–14229.
- Qin, B., Zhu, G., Gao, G., Zhang, Y., Li, W., Paerl, H.W., Carmichael, W.W., 2010. A drinking water crisis in Lake Taihu, China: linkage to climatic variability and lake management. *Environ. Manage.* 45, 105–112. doi:10.1007/s00267-009-9393-6
- Watson, S.B., Monis, P., Baker, P., Giglio, S., 2016. Biochemistry and genetics of taste- and odor-producing cyanobacteria. *Harmful Algae, Global Expansion of Harmful Cyanobacterial Blooms: Diversity, ecology, causes, and controls* 54, 112–127. doi:10.1016/j.hal.2015.11.008

Tables

Table 1. Pitcher-style water purifiers used in this study and their contact time in seconds per L (the length of time for 1 L of tap water to percolate through each filter cartridge) and their advertised source of activated carbon. Values are mean \pm 1 SE of 3 separate filter cartridges.

| Purifier | Contact time (seconds/L) | Activated Carbon | Identifier for this report |
|-----------|--------------------------|------------------|----------------------------|
| Brand "A" | 125.9 \pm 2.41 | Coconut | 126-purifier |
| Brand "B" | 230.9 \pm 7.30 | "Blend" | 231-purifier |
| Brand "C" | 374.0 \pm 2.41 | "Blend" | 374-purifier |

Table 2. Microcystin congeners as percent of total in the *Microcystis*-extracted and *Planktothrix*-extracted experiments. "ND" indicates non-detect due to concentration below the method detection limit of 0.01 to 0.05 ppb for each congener.

| Microcystin- | <i>Microcystis</i> | <i>Planktothrix</i> |
|----------------------------|--------------------|---------------------|
| [DAsp ³] MC-RR | ND | ND |
| MC-RR | 45.45% | 75.00% |
| MC-YR | 22.73% | 12.50% |
| MC-HtyR | 4.54% | ND |
| MC-LR | 27.27% | 6.25% |
| [DAsp ³] MC-LR | ND | 6.25% |
| [Dha ⁷] MC-LR | ND | ND |
| MC-HiIR | ND | ND |
| MC-WR | ND | ND |
| [DLeu ¹] MC-LR | ND | ND |
| MC-LA | ND | ND |
| MC-LY | ND | ND |
| MC-LW | ND | ND |
| MC-LF | ND | ND |

Figures

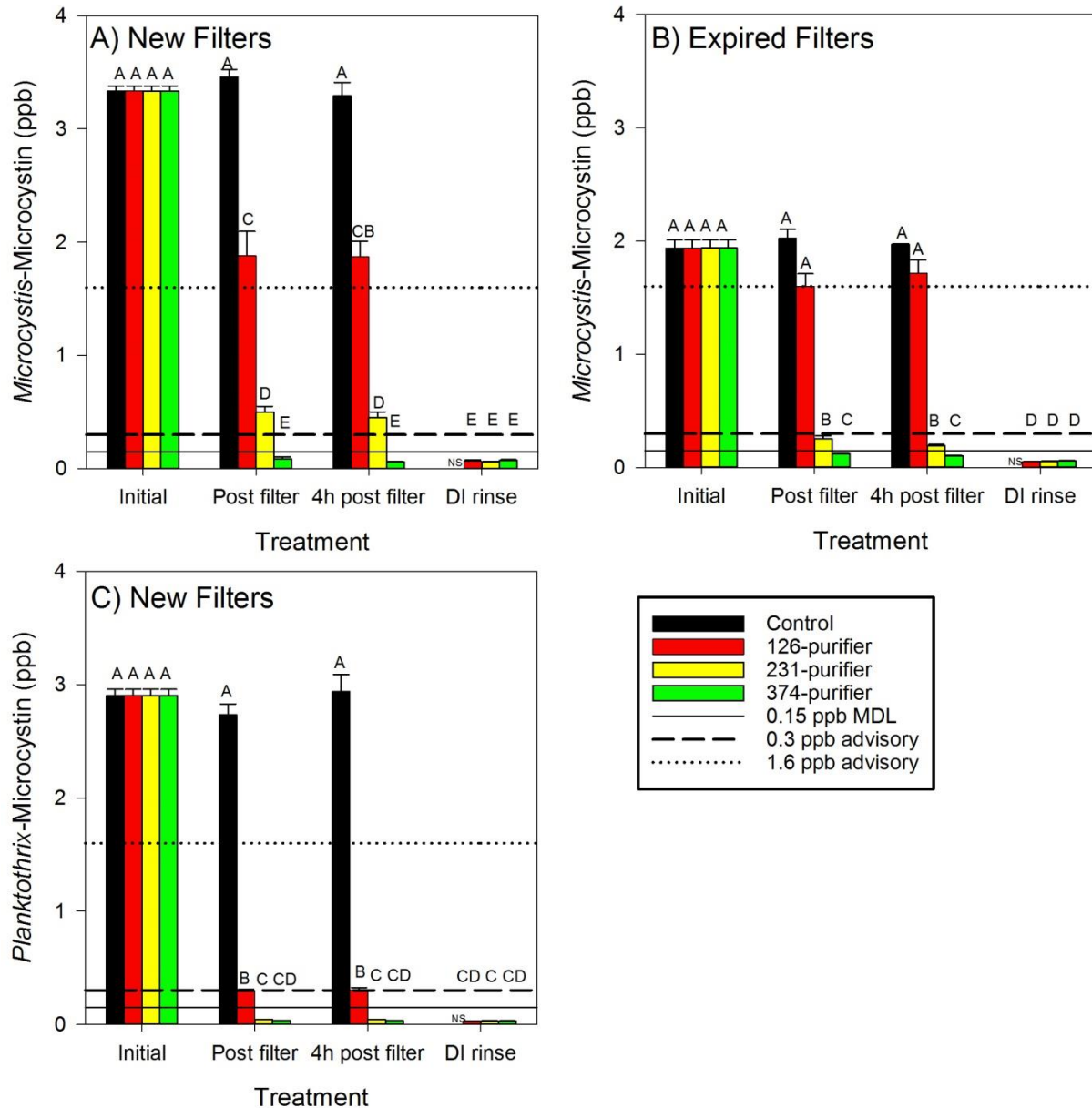


Figure 1. Microcystin concentration (parts per billion) immediately following percolation through pitcher-style purifiers (“post filter”), 4 hours after percolation, and in deionized water percolated through the purifiers after the microcystin-laden water was discarded (“DI rinse”). Experiments were conducted with microcystin extracted from *Microcystis* (A, B) and *Planktothrix* (C). Bars are means (± 1 standard error) of 3 replicate pitchers. Letters above bars are Tukey test results with mean of A > B > C. Horizontal lines indicate the method detection limit, the 1.6 ppb advisory level for adults, and the 0.3 ppb advisory level for children. “NS” = no sample. DI water was not poured into the non-filtered controls and analyzed.

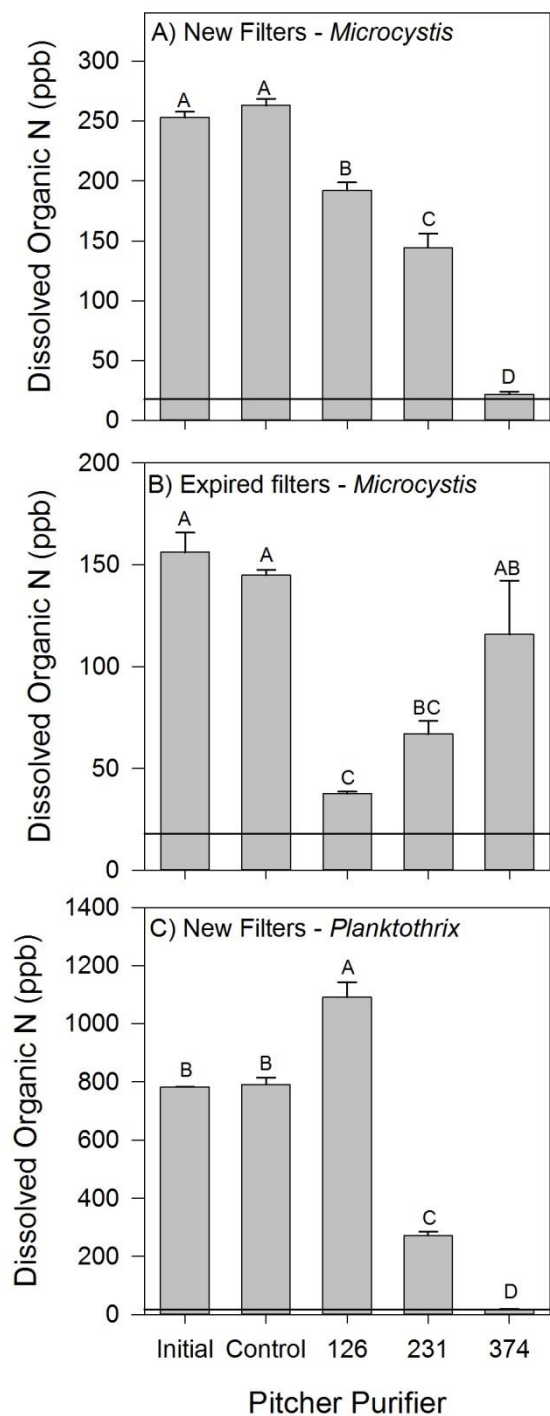


Figure 2. Dissolved organic nitrogen concentration in water that percolated through pitcher-style purifiers and extracted from extracted from *Microcystis* (A, B) and *Planktothrix* (C). Bars are means (± 1 standard error) of 3 replicate pitchers. Letters above bars are Tukey test results with mean of $A > B > C$. Horizontal line indicate the method detection limit.

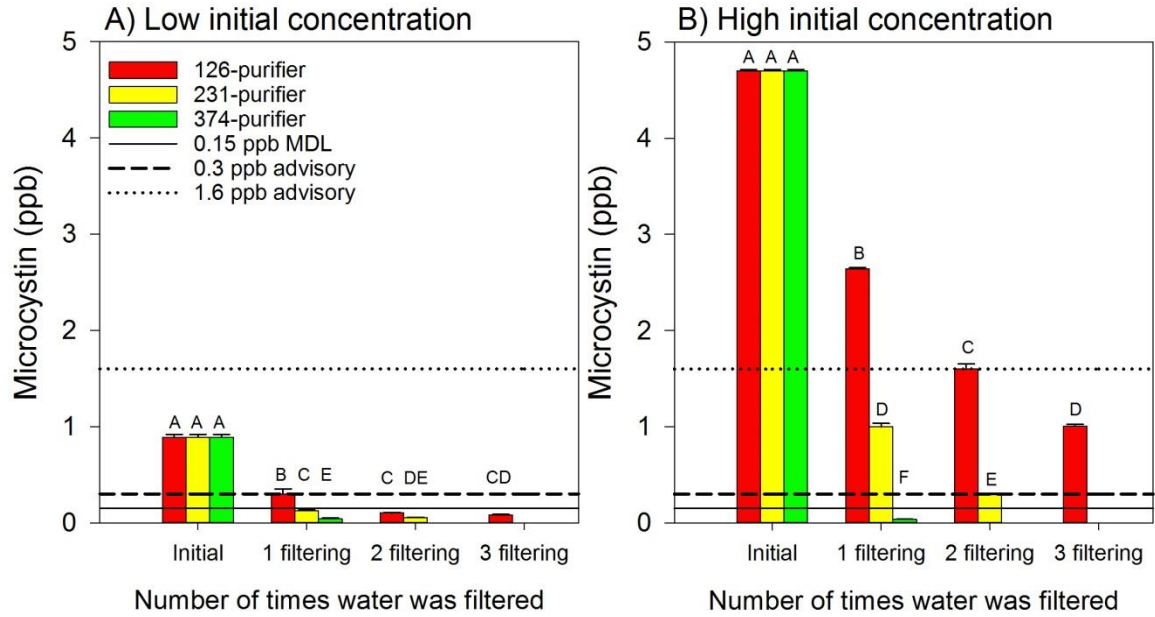


Figure 3. Microcystin concentration in the two repeated filtering experiments. Water subjected to the 126-purifier was percolated through the same purifier 3 times, the 231-purifier twice, and the 374-purifier just once. Bars are means (± 1 standard error) of 3 replicate pitchers. Letters above bars are Tukey test results with mean of $A > B > C$. Horizontal lines indicate the method detection limit, the 1.6 ppb advisory level for adults, and the 0.3 ppb advisory level for children.

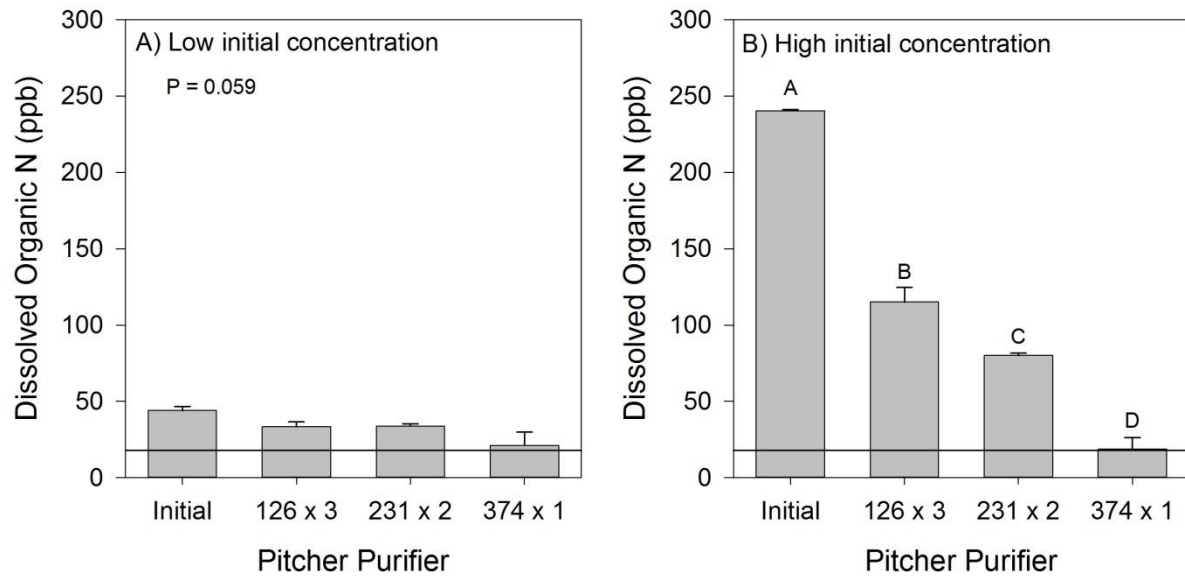


Figure 4. Final dissolved organic nitrogen concentration in water that was subjected to the 126-purifier 3 times, the 231-purifier twice, and the 374-purifier once. DON was not measured after each percolation step (as in Figure 3). Bars are means (± 1 standard error) of 3 replicate pitchers. Letters above bars are Tukey test results with mean of $A > B > C$. Horizontal line indicate the method detection limit.