The ability of household pitcher-style water purifiers to remove microcystins depends on filtration rate and activated carbon source

Justin D. Chaffin, Erica L. Fox, Callie A. Nauman and Kristen N. Slodysko

ABSTRACT

Toxic cyanobacterial blooms are a global threat to human health due to contamination of drinking water. To ensure public safety, water treatment plants must have the capability to remove cyanotoxins from water. Recently, however, there have been several instances when microcystins, a common group of cyanotoxins, have been detected in tap water. This research investigated if commercially available pitcher-style water purifiers were able to remove microcystins from water. Microcystins were extracted from two naturally occurring blooms in Lake Erie, diluted to initial concentrations ranging from 1 to 5 μg/L, and then subjected to three purifier types. Results showed that the purifier with the fastest percolation rate (126 seconds/L) and a filter cartridge comprised solely of coconut-based activated carbon removed 50% or less of the microcystins, while the purifier with the slowest percolation rate (374 seconds/L) and a blend of activated carbon decreased microcystins to below detectable levels (<0.10 μg/L) in all experiments. Thus, pitcher-style purifiers with slow percolation rates and composed of a blend of active carbon can provide an additional layer of protection against microcystins; however, it is recommended that consumers switch water sources when cyanotoxins are confirmed to be in tap water.

Key words | cyanobacteria, Lake Erie, microcystins, toxins, water treatment

Justin D. Chaffin (corresponding author)
Erica L. Fox
Callie A. Nauman
Kristen N. Slodysko
F.T. Stone Laboratory,
The Ohio State University,
878 Bayview Ave., Put-in-Bay, OH 43456,
USA
E-mail: *chaffin.46@osu.edu*

Callie A. Nauman
Aquatic Ecology Laboratory,
The Ohio State University,
Columbus, OH 43210,
USA

Kristen N. Slodysko
Department of Environmental Science,
State University of New York College of
   Environmental Science and Forestry,
Syracuse, NY 13210,
USA

INTRODUCTION

Toxin-producing, freshwater cyanobacterial blooms have become a global threat to the safety of drinking water (Qin *et al.* 2010; Roegner *et al.* 2013; He *et al.* 2016). Cyanobacteria have the potential to produce several 'cyanotoxins' that negatively impact multiple organ systems of vertebrates, including humans (Carmichael 1992). Microcystins, a group of >100 cyclic peptide congeners, are one of the most potent and commonly produced cyanotoxins. Microcystins were responsible for the August 2014 'do not drink' advisory in Toledo, Ohio, that left more than 400,000 residents

without potable tap water for 3 days (Jetoo *et al.* 2015). Many Toledo residents continue to consume only bottled water, although microcystins have not been detected in Toledo's tap water since August 2014 (Larson 2017). 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 (Paerl *et al.* 2016). Recent improvements in land use and sewage treatment are ongoing to prevent blooms, but in the meantime, the ability to remove microcystins from surface water to ensure public safety is crucial.

The majority of research conducted regarding removing microcystins from drinking water has occurred at the water

treatment plant scale. Conventional methods include activated carbon (Ho *et al.* 2011), UV light and hydrogen peroxide oxidation (He *et al.* 2012), and ozone (Hitzfeld *et al.* 2000). If microcystins break through water plant treatment, the distribution system will send the cyanotoxins to consumers; however, the fate of microcystins in the distribution system is not understood. Point-of-use treatment options are the last layer of defense against microcystins for consumers concerned about cyanotoxins in tap water (Roegner *et al.* 2013). For example, Pawlowicz *et al.* (2006) showed that carbon-based under-the-sink filters connected to a faucet would remove more than 99.7% of microcystins spiked into deionized water. However, they also showed that pleated paper and string wound filters allowed more than 90% of microcystins to pass through (Pawlowicz *et al.* 2006). Thus, the effectiveness of the filters depends on composition and design. The ability of point-of-use filters, such as pitcher-style water purifiers, to remove microcystins from water has not been tested; however, they may provide consumers concerned about microcystins an additional layer of protection.

The objective of this project was to determine if household pitcher-style water purifiers are effective at removing microcystins from water. Microcystins extracted from two natural Lake Erie cyanobacterial blooms (*Microcystis* and *Planktothrix* blooms) were subjected to the pitcher purifier treatment. Initial concentrations of total microcystins in these experiments were between 0.8 and 5.0 µg/L, which spans the range of likely microcystins concentrations in Toledo's tap water during the 2014 crisis (Qian *et al.* 2015). This method replicates a more realistic scenario than spiking pure microcystins in deionized water because water treatment plants draw in lake water that contains natural organic matter (NOM) in addition to potentially toxic cyanobacteria. Furthermore, it is likely that if microcystins break through the treatment process, NOM will as well. This is supported by taste and odor issues in drinking water, which are associated with the metabolite products of algal blooms (Watson *et al.* 2016). Additionally, NOM competes with microcystins for adsorption sites on activated carbon (Lambert *et al.* 1996). Dissolved organic nitrogen (DON) was quantified as a proxy for dissolved organic compounds, other cyanotoxins, and taste and odor compounds. Additionally, repeated filtering through the purifiers was tested to determine if increased filter contact

time could improve removal of microcystins. Finally, the experiment was repeated with expired filters to determine if microcystin removal was affected by repeated filter usage because activated carbon, the primary component of the water filters, has a limited adsorption capacity for contaminants (Huang *et al.* 2007; Wang *et al.* 2007).

METHODS

Water purifiers

Three different purifier brands were tested in this research, and the components of each brand's filter cartridge were unique (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 three purifier brands were certified by NSF International/American National Standards Institute standards #42 and #53 for health and aesthetic effects; however, microcystins were not included in the certification. These purifiers are commercially available and can be purchased at a local supermarket. 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 (nine total pitchers), and water poured into pint glasses served as a non-purified control.

New filter cartridges were installed according to manufacturer instructions. To determine if the filter cartridges could produce a false positive for microcystins, 1 L of deionized (DI) water was poured through each purifier, which was sampled for microcystins after percolating into the reservoir. All samples in this test were below the detection limit. Additionally, pH and chloride concentrations were measured and verified to be within the range specified by the microcystins enzyme-linked immunosorbent assay (ELISA) kit (pH between 5 and 11, Cl < 0.10 mg/L), so as not to interfere with the assay.

Microcystins collection and experiment preparation

Ten 2 L samples of Lake Erie water containing microcystin-producing *Microcystis* were collected on 24 July 2015 from Put-in-Bay during a surface scum, and two 10 L samples

Table 1 | Pitcher-style water purifiers used in this study, measured contact time in seconds per L (the length of time for 1 L of tap water to percolate through each filter cartridge), components of the filter cartridge listed by the manufacturer, and dry weight of the cartridge

Purifier	Brand 'A'	Brand 'B'	Brand 'C'
Contact time (seconds/L)	125.9 ± 2.41	230.9 ± 7.30	374.0 ± 2.41
Identifier for this report	126-purifer	231-purifier	374-purifier
NSF/ANSI Certification Standards	#42 & #53	#42 & #53	#42
Activated carbon base	Coconut	'Blend'	'Blend'
Ion exchange	Yes	Yes	Yes
Coarse filter	X	X	Yes
Distributor to slow water	X	X	Yes
Membrane	X	X	Yes
Organization of components	Mixture of granules	Vertical rings	Layered horizontally
Dry weight (g)	83.4 ± 0.07	129.78 ± 2.02	451.27 ± 6.98

'X' indicates that the component was not listed as a filter cartridge component. Values of contact time are mean ± 1 SE of 3 separate filter cartridges.

were collected on 10 August 2015 from Sandusky Bay during a *Planktothrix* bloom. The samples were observed under a microscope at 100× magnification to confirm the genera present. *Microcystis* was the only genera observed in the Put-in-Bay sample, while the Sandusky Bay sample was nearly 100% *Planktothrix* with a few colonies of *Dolichospermum* (*Anabaena*) and *Aphanizomenon* observed. The water samples were subjected to three freeze/thaw cycles to lyse cells and extract microcystins, and the concentration was measured using ELISA (see below). After total microcystins concentrations were measured, the water was held at $-20\,^{\circ}$C until experimentation. On the day of an experiment, water was thawed (four total freeze/thaw cycles), filtered through glass fiber filters (0.45 μm) to remove cellular debris, and diluted in a 20 L carboy with DI water to lower the total microcystins concentration to a range of 1 to 5 μg/L. Samples for initial measurements of total microcystins and DON concentrations were collected from a 1 L subsample.

Experimental methods

In the experiment testing filter compositions, 1 L of water containing microcystins was poured into each purifier. Samples were collected from the purifier's reservoir beneath the filter cartridge immediately after all of the 1 L percolated through the filter cartridge. Each purifier was subsampled three times for microcystins by pipetting 10 mL of water from the pitcher purifier into three separate amber glass

vials (results from these subsamples were averaged to determine total microcystins concentration for that purifier). A 150 mL sample was poured from the pitcher into a 250 mL polycarbonate bottle for DON analysis. Then, the purifiers were resampled 4 hours after initial percolation to determine if the filter cartridges leaked microcystins back into the water. Finally, the water was discarded from the pitcher, and 1 L of DI water was poured into the purifier and sampled to determine if microcystins became unbound from the filter cartridge. These experiments were conducted with new filter cartridges and with water from the Lake Erie *Microcystis* and *Planktothrix* blooms. An additional experiment was conducted to test expired filter cartridges following the above method and utilized the *Microcystis*-microcystins water. Local tap water was poured through filters until the cartridge was considered to be expired according to manufacturer guidelines, and all manufacturers indicated that the capacity was approximately 150 L per cartridge. This cartridge capacity indicates that a family of four that consumes 2.5 L/person/day would need to replace the cartridge every 15 days.

Because percolation rates differed remarkably among the three types of purifiers (see results, Table 1), which introduced a contact time bias into the study, another experiment was designed to determine if increased filter contact time would increase microcystins and DON removal. In separate experiments using new filter cartridges, 1 L of *Microcystis*-microcystins water was poured into each purifier and sampled for microcystins as above. The filtered

water was poured from the purifier into a clean glass beaker, then back into the purifier to percolate through the filter cartridge for a second time, after which a microcystins sample was collected. This process was repeated for a third time. Water for DON analysis was only sampled after the final purification step. This experiment was conducted twice, once using water with an initial total microcystins concentration of 0.96 μg/L and then again with an initial concentration of 4.8 μg/L.

Quantification analysis and QC criteria

Total microcystins analysis began immediately after sample collection and utilized the ELISA following Ohio EPA protocol #701.2 with Abraxis kits (#520011, Warminster, USA). The ELISA method is not specific to any one microcystin congener, and the method had good cross-reactivity among microcystin congeners tested (according to the Abraxis user guide). For this reason, all ELISA measurements quantify the total microcystins concentration. For all ELISA results accepted in this research, the R^2 values between known concentration standards (0.0 to 5.0 μg/L) and measured absorbance were 0.98 or greater. All standards and samples were analyzed in duplicate and coefficients of variation between duplicates were less than 10%. Laboratory reagent blanks were all below the method detection limit (MDL) of 0.10 μg/L (as established by Abraxis). The low calibration range checks (0.4 μg/L) and the quality control standard (0.75 μg/L) were within acceptable ranges, according to Ohio EPA protocol #701.2. Analysts certified by the Ohio EPA conducted all ELISA tests.

DON was quantified as ammonia after Kjeldahl digestion on a SEAL Analytical QuAAttro continuous segmented flow analyzer, following standard method EPA 351.2. All DON samples were analyzed in duplicate. The R^2 values between known concentration standards (0.0 to 1,400.0 μg N/L) and measured absorbance were greater than 0.99. A solution of 700 μg urea-N/L was analyzed for every batch as the quality control standard and results were within ±10%. Every tenth sample was spiked with a known amount of analyte to ensure high accuracy and precision throughout the analysis (>95% recovery). The high standard and the zero standard were analyzed every 20th sample to check for and correct for instrument drift. The MDL was 18 μg N/L.

Data analysis

Many of the samples analyzed with ELISA gave total microcystins concentrations below detectable concentrations (<0.10 μg/L). However, ELISA will always estimate a concentration value, typically around 0.05 μg/L, even for laboratory reagents blanks (DI water) which have zero microcystins. The estimated concentrations were used to calculate treatment averages, even for occurrences where the value was less than the MDL. Analysis of variance (ANOVA) with a post hoc Tukey test was used to determine differences among treatments.

RESULTS

Percolation rates

Filter contact times were remarkably different among the three 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 (Table 1). These contact times were converted to percolation rates to give 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). However, it is important to note that contact time was not the only variable that affected microcystins removal because the purifiers had different components (see discussion).

Microcystins removal

Figures in the results section display the treatment averages of the estimated total microcystins concentration. While values less than the MDL were included, the actual total microcystins concentration could range from zero to 0.10 μg/L. Hence, it could not be confirmed or denied that the purifiers removed 100% of the microcystins.

Initial total microcystins concentration in the *Microcystis*-extracted water was 3.3 μg/L (Figure 1(a)). Total microcystins concentration significantly decreased (*P* < 0.001) following percolation through each purifier, but was detected in the filtered water from two of the three purifiers (Figure 1(a)). The 126-purifier decreased total microcystins
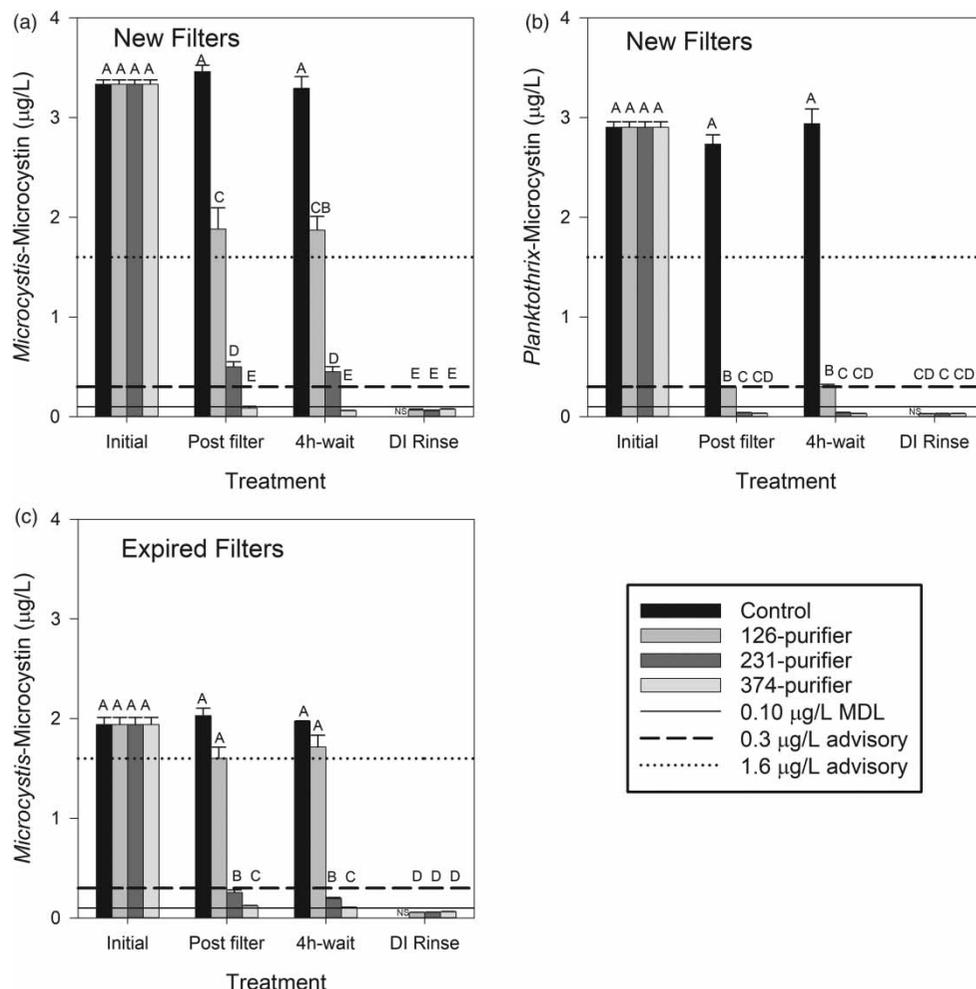
Figure 1 | Total microcystin concentration (μg/L) following percolation through pitcher-style purifiers ('post filter'), 4 hours after percolation ('4h-wait'), and in deionized water percolated ('DI rinse'). Experiments were conducted with new filter cartridges with microcystins extracted from (a) *Microcystis* and (b) *Planktothrix* and (c) with expired cartridges using *Microcystis*-microcystins. Bars are means (±1 standard error) of three replicate pitchers. Letters above bars are Tukey test results with mean of A > B > C > D > E. Horizontal lines indicate the method detection limit, advisory level for children, and the advisory level for adults. 'NS' = no sample. DI water was not poured into the non-filtered controls.

to 1.88 ± 0.21 μg/L and the 231-purifier decreased microcystins to 0.50 ± 0.05 μg/L. Microcystins were decreased to non-detectable levels by the 374-purifier. Total microcystins concentration in the filtered water did not change 4 hours after percolation, and microcystins were not detected in DI water that was filtered through the purifiers. *Planktothrix*-extracted microcystins had an initial concentration of 2.90 μg/L (Figure 1(b)). The 126-purifier decreased total microcystins to 0.28 ± 0.03 μg/L, while the 231- and 374-purifiers decreased microcystins to below detectable levels. Again, the total microcystins concentrations did not change after 4 hours and were not detectable following a DI water flush. The expired filter cartridge experiment

with *Microcystis*-extracted microcystins had an initial concentration of 1.94 μg/L (Figure 1(c)). Following percolation, water from the 126-purifier was significantly similar to the non-filtered control ($P > 0.05$). The 231-purifier decreased total microcystins to 0.25 ± 0.03 μg/L and the 374-purifier decreased microcystins to non-detectable levels. Again, the total microcystins concentrations did not change after 4 hours and were not detectable following a DI water flush.

Water percolated through the 126-purifier nearly three times as fast as the 374-purifier. Water from the 126-purifier was filtered three times in total (refiltered two times after initial contact) to increase contact time to a similar contact time as the 374-purifier. The filter with the intermediate contact time
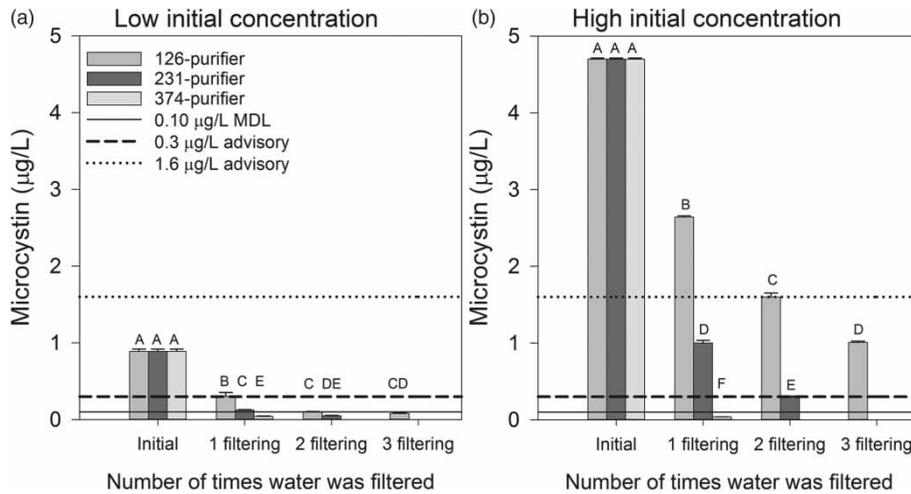
Figure 2 | Total microcystins concentration in the two repeated filtering experiments, (a) with low initial concentration and (b) with high initial concentration. Water was percolated through the 126-purifiers three times, the 231-purifiers twice, and the 374-purifiers just once. Bars are means (±1 standard error) of three replicate pitchers. Letters above bars and horizontal lines follow the Figure 1 caption.

of 231 seconds/L was filtered twice. Therefore, this experiment standardized contact time among the three purifiers. Initial concentrations for the two experiments conducted were 0.89 µg/L (Figure 2(a)) and 4.70 µg/L (Figure 2(b)) of *Microcystis*-extracted microcystins. The 374-purifier decreased microcystins to below detectable levels in both the low and high initial microcystin experiment after one time percolation (Figure 2). The 231- and 126-purifiers decreased total microcystins concentrations in a step-wise fashion, but the 231-purifier decreased microcystins more than the 126-purifier. In the high microcystins experiment, the 231-purifier decreased total microcystins to 1.00 ± 0.03 µg/L after one percolation then to 0.29 ± 0.02 µg/L after two percolations, while the 126-purifier decreased total microcystins to 2.64 ± 0.01 µg/L, 1.60 ± 0.05 µg/L, and 1.01 ± 0.02 µg/L, respectively, after each percolation step (Figure 2(b)).

DON removal

In the new filter *Microcystis*-extracted experiment, the initial DON concentration was 252.9 µg/L and the 126-, 231-, and 374-purifier significantly ($P < 0.001$) decreased DON to 191.9 ± 6.7 µg/L, 144.2 ± 11.9 µg/L, and 21.9 ± 2.1 µg/L, respectively (Figure 3(a)). Initial DON of the *Planktothrix*-extracted experiment was much higher than the *Microcystis*-extracted water at 782.5 µg/L (Figure 3(b)). DON concentration increased following percolation through the 126-purifier,

while the 231- and 374-purifier decreased DON to 272.5 ± 12.5 µg/L and 18.0 ± 2.2 µg/L, respectively (Figure 3(b)). In the expired *Microcystis*-extracted experiment, the 126-purifier decreased DON to the lowest levels while the water of the 374-purifier had significantly similar DON concentration as the non-filtered control (Figure 3(c)). DON was not measured following the 4-hour wait and after the DI flush.

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 ($P = 0.059$; Figure 4(a)). Initial DON concentration was 240.4 µg/L in the high experiment (Figure 4(b)). After three-time percolation through the 126-purifier, DON was reduced to 115.0 ± 9.60 µg/L, while two-time percolation through the 231-purifier reduced DON to 80.0 ± 1.45 µg/L. DON concentration was reduced to 19.0 ± 7.39 µg/L after one-time percolation through the 374-purifier.

DISCUSSION

It has been forecast that toxic cyanobacterial blooms will increase in magnitude under current climate change scenarios (Paerl *et al.* 2016). Therefore, it is paramount that all possible actions (land use and water treatment actions) are taken to remove cyanobacterial toxins from water to provide
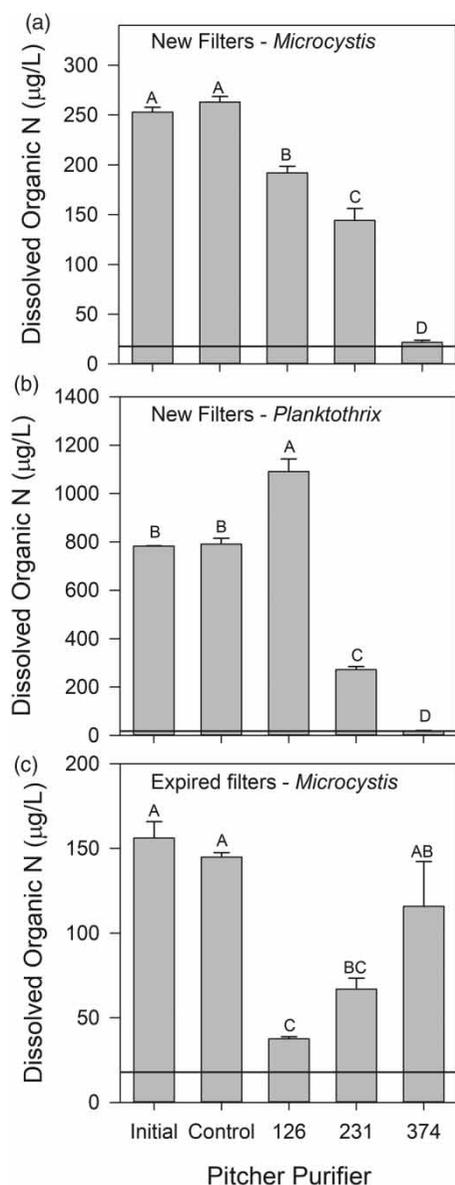
Figure 3 | DON concentration in water that percolated through new filter cartridges with organic matter extracted from (a) *Microcystis* and (b) *Planktothrix* and (c) through expired cartridges with *Microcystis*-extracted organic matter. Bars are means (±1 standard error) of three replicate pitchers. Letters above bars are Tukey test results with mean of A > B > C > D. Horizontal line indicates the method detection limit.

safe drinking water. A common question asked of scientists who study cyanobacteria and of 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 could add another layer of defense against microcystins; however, the amount of microcystins removed varied among different purifiers.

Activated carbon is a significant component of all three filter cartridges tested and is one of the several methods used by water treatment plants to remove dissolved organics, including microcystins, from drinking water (as reviewed by He *et al.* 2016). Electrostatic and hydrophobic interactions between microcystins and activated carbon result in toxin adsorption and removal from water (He *et al.* 2016). There are several sources of activated carbon (wood, coal, coconut, peat moss) and their efficiency in removing 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, and microcystins, which are in the 1–3 nm range, are more effectively adsorbed by mesopores (Westrick *et al.* 2010; Roegner *et al.* 2013). Coconut produces micropores, whereas wood produces both micropores and mesopores. Indeed, previous batch experiments have shown that wood-based activated carbon has the highest microcystin removal efficiency (Donati *et al.* 1994; Pendleton *et al.* 2001; Roegner *et al.* 2013). The 126-purifier used coconut shells as the carbon source, and therefore, the 126-purifier is not well suited to removing microcystins due to the lack of mesopores. The 231- and 374-purifiers advertise that a 'blend' of activated carbon was used; however, the composition of these carbon blends was unknown.

In addition to the activated carbon, the ability of each purifier to remove microcystins was also a function of percolation rates. The purifier with the quickest percolation (lowest contact time) removed the least amount of microcystins, whereas the purifier with the slowest percolation (greatest contact time) decreased microcystins to below detectable levels in all experiments. The experiments with repeated percolations suggested that more microcystins would have been removed by the 126- and 231-purifiers if they had longer contact times. This result agrees with previous batch adsorption experiments that have shown the binding capacity of activated carbon is a function of contact time (Namasivayam & Kavitha 2002; Hameed *et al.* 2007; Huang *et al.* 2007). However, after the third time the microcystins-water was poured through the 126-purifier (total contact time of 378 seconds/L) the total microcystins concentration was still 1.0 µg/L, which was unlike the one-time percolation of the 374-purifier
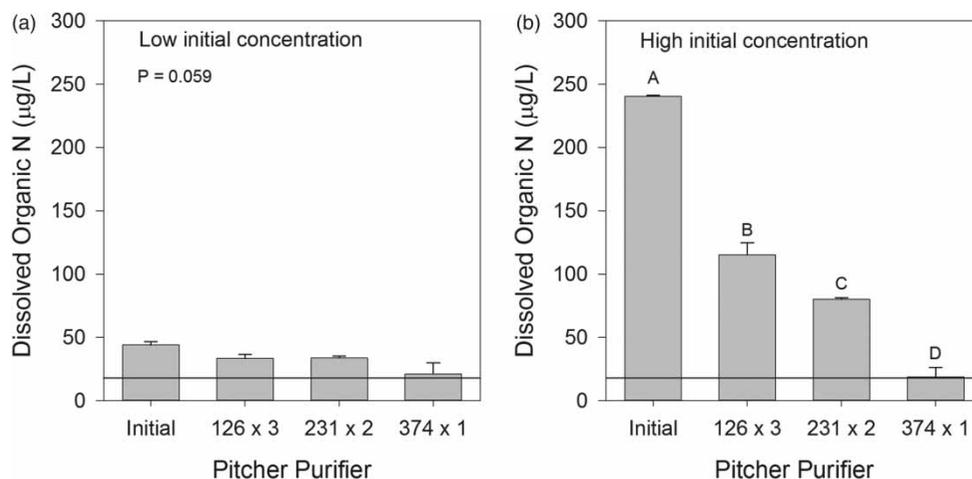
Figure 4 │ Final DON concentration in water that was subjected to the 126-purifier three times, the 231-purifier twice, and the 374-purifier once. DON was not measured after each percolation step (as in Figure 2). Bars are means (±1 standard error) of three replicate pitchers. Letters above bars and horizontal lines follow the Figure 3 caption.

which decreased microcystins to below detectable levels. This result indicated that the contents of the filter cartridges also impacted microcystins removal.

Total microcystins concentration did not differ between samples collected immediately after percolation and 4 hours after percolation (Figure 1). Furthermore, microcystins were not detected in DI water that was percolated through the purifiers. These results indicated that microcystins bound to the activated carbon did not become unbound with repeated use. These results were true for both new and expired filter cartridges of the 231- and 374-purifiers. However, the expired 126-purifiers did not significantly decrease microcystins (Figure 1(c)), which was likely due to activated carbon's limited adsorption capacity for contaminants (Hameed *et al.* 2007; Huang *et al.* 2007; Wang *et al.* 2007). The adsorption sites will become saturated with increased use and will result in the inability to remove contaminants from the water (Dvorak & Skipton 2013; Roegner *et al.* 2013). It was likely that the expired 126-purifier's coconut-based activated carbon became saturated with NOM, which allowed microcystins to break through.

Microcystins are a widespread group of toxins produced by many different bloom-forming cyanobacteria genera, but cyanobacteria can produce many other harmful toxins, such as anatoxins, saxitoxins, and cylindrospermopsins (Huisman *et al.* 2010). However, the results of this study cannot be extrapolated to the other cyanotoxins due to the different molecular sizes (anatoxin-a 165 g/mol, saxitoxin

300 g/mol, cylindrospermopsin 415 g/mol, microcystins 900–1,050 g/mol) (Carmichael 1992; Ho *et al.* 2011) and the efficiency of different activated carbons at removing different sizes of organic molecules. For example, Ho *et al.* (2011) showed that the adsorption of cylindrospermopsins and microcystins by coal-based powdered activated carbon differed at short contact times; however, Ho *et al.* (2011) also showed that with increased contact time both cyanotoxins were effectively 100% removed from water.

DON was quantified as a proxy for dissolved organic compounds and other cyanotoxins. While microcystins are N-rich (14% by mass), microcystin-N was a small percentage of the DON. For example, a total microcystin concentration of 4.8 µg/L (Figure 2(b)) converts to 0.67 µg N/L or 0.3% of the DON. The large nitrogenous organic compounds (proteins, nucleic acids, pigments) released from the lysed cyanobacterial cells would likely be adsorbed by the mesopores in activated carbon of the 231- and 374-purifiers by similar mechanisms as microcystins, but micropores could adsorb smaller compounds in coconut-based activated carbon. Additionally, the ion exchange resins would remove ions of nitrogen. In general, DON concentration in the filtered water followed the same pattern as microcystins, especially among the new filters (Figures 3(a), 3(c) and 4), and indicates that the 374-purifier was the most efficient purifier for removing DON. However, there were two exceptions to this general pattern. First, the 126-purifier increased DON from its initial concentration in the *Planktothrix*

experiment (Figure 3(b)). Additionally, the expired 126-purifier cartridges removed a higher percentage of DON than the new 126-purifier cartridges. These unexpected results cannot be explained. Secondly, the expired 374-purifier resulted in DON concentrations that were not significantly different from initial concentrations (Figure 3(c)). In this case, it is possible that the smaller pores and/or ion exchange became saturated, which allowed DON to pass through, but there could have been free spaces in mesopores that adsorbed microcystins. Overall, these results suggest that new cartridges of the 374-purifier have the highest potential to remove other cyanotoxins from water, but additional research is needed for confirmation.

When microcystins have 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 total microcystins are 0.3 µg/L for children and 1.6 µg/L for adults. Only one of the three purifiers tested in this research decreased total microcystins to less than 0.3 µg/L in all tests. Furthermore, due to the relatively high MDL of ELISA (0.10 µg/L), it is unknown if the 374-purifier removed all of the microcystins. Therefore, when microcystins are 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 and instead purchase bottled water (Larson 2017), activated carbon pitcher-style water purifiers would be a more economical and less-wasteful 'safety net' option than bottled water. While there are other point-of-use water treatment options, pleated paper and string-wound filters or media containing halogenated bromine or chlorine are less effective at removing microcystins from water (Pawlowicz et al. 2006; Coulliette et al. 2010). Therefore, it is critical that activated carbon filters, and ideally not coconut-based, are utilized for the goal of removing microcystins.

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 microcystins to concentrations less than 0.3 µg/L (NSF International 2016). Results from this study indicate only the 374-purifier would achieve that certification. However, the lower the initial total microcystins concentration, the higher the chance that any

purifier can decrease total microcystins to 0.3 µg/L. For example, the 126-purifier achieved 0.3 µg/L when the initial total microcystins concentration was 0.89 µg/L (Figure 2(a)), but the 126-purifier did not achieve 0.3 µg/L when initial total microcystins concentration was 1.9 µg/L or greater (Figures 1(a)–1(c) and 2(b)).

CONCLUSIONS

In conclusion, the amount of microcystins removed by point-of-use pitcher-style purifiers differed by type of filter cartridge. The purifier that was most effective at removing microcystins had the slowest percolation time and a cartridge consisting of a blend of activated carbon, whereas the purifier with the quickest rate of percolation and coconut-based activated carbon removed the least amount of microcystins. Because cyanobacterial blooms will likely persist in the near future, pitcher-style water purifiers may provide consumers with an additional layer of protection against microcystins. Nonetheless, it is still recommended that consumers switch water sources during times when microcystins are known to be present in tap water.

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REFERENCES

Carmichael, W. W. 1992 Cyanobacteria secondary metabolites – the cyanotoxins. Journal of Applied Bacteriology 72 (6), 445–459. https://doi.org/10.1111/j.1365-2672.1992.tb01858.x.

Coulliette, A. D., Peterson, L. A., Mosberg, J. A. W. & Rose, J. B. 2010 Evaluation of a new disinfection approach: efficacy of chlorine and bromine halogenated contact disinfection for reduction of viruses and microcystin toxin. *The American Journal of Tropical Medicine and Hygiene* **82** (2), 279–288. https://doi.org/10.4269/ajtmh.2010.09-0279.

Donati, C., Drikas, M., Hayes, R. & Newcombe, G. 1994 Microcystin-LR adsorption by powdered activated carbon. *Water Research* **28** (8), 1735–1742. https://doi.org/10.1016/0043-1354(94)90245-3.

Dvorak, B. I. & Skipton, S. 2013 Drinking water treatment: activated carbon filtration. *Water Resource Management Drinking Water* **11**, 1–12.

Hameed, B. H., Din, A. T. M. & Ahmad, A. L. 2007 Adsorption of methylene blue onto bamboo-based activated carbon: kinetics and equilibrium studies. *Journal of Hazardous Materials* **141** (3), 819–825.

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/H$_2$O$_2$ in synthetic and natural water samples. *Water Research* **46** (5), 1501–1510. https://doi.org/10.1016/j.watres.2011.11.009.

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. https://doi.org/10.1016/j.hal.2016.01.001.

Hitzfeld, B. C., Höger, S. J. & Dietrich, D. R. 2000 Cyanobacterial toxins: removal during drinking water treatment, and human risk assessment. *Environmental Health Perspectives* **108** (Suppl. 1), 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 Research* **45** (9), 2954–2964. https://doi.org/10.1016/j.watres.2011.03.014.

Huang, W. J., Cheng, B. L. & Cheng, Y. L. 2007 Adsorption of microcystin-LR by three types of activated carbon. *Journal of Hazardous Materials* **141** (1), 115–122. https://doi.org/10.1016/j.jhazmat.2006.06.122.

Huisman, J., Matthijs, H. C. P. & Visser, P. M. (eds) 2010 *Harmful Cyanobacteria* (softcover reprint of hardcover 1st edn 2005). Springer, Dordrecht, The Netherlands.

Jetoo, S., Grover, V. I. & Krantzberg, G. 2015 The Toledo drinking water advisory: suggested application of the water safety planning approach. *Sustainability* **7** (8), 9787–9808. https://doi.org/10.3390/su7089787.

Lambert, T. W., Holmes, C. F. B. & Hrudey, S. E. 1996 Adsorption of microcystin-LR by activated carbon and removal in full scale water treatment. *Water Research* **30** (6), 1411–1422.

Larson, D. 2017 City insists tap water is safe as consumers stockpile bottled water. Toledo ABC News. http://www. 13abc.com/content/news/City-continues-to-insist-water-is-safe-as-consumers-stockpile-bottled-water-448532943.html (accessed 4 April 2018).

Namasivayam, C. & Kavitha, D. 2002 Removal of Congo Red from water by adsorption onto activated carbon prepared from coir pith, an agricultural solid waste. *Dyes and Pigments* **54** (1), 47–58. https://doi.org/10.1016/S0143-7208(02)00025-6.

NSF International 2016 NSF International certifies first water filters that reduce microcystin in drinking water. http://www.nsf.org/newsroom/nsf-international-certifies-first-water-filters-that-reduce-microcystin-in (accessed 15 March 2016).

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. https://doi.org/10.1016/j.hal.2015.09.009.

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. *Journal of Water and Health* **4** (1), 99–107.

Pendleton, P., Schumann, R. & Wong, S. H. 2001 Microcystin-LR adsorption by activated carbon. *Journal of Colloid and Interface Science* **240** (1), 1–8. https://doi.org/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. *Environmental Science & Technology* **49** (24), 14221–14229. https://doi.org/10.1021/acs.est.5b03029.

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. *Environmental Management* **45** (1), 105–112. https://doi.org/10.1007/s00267-009-9393-6.

Roegner, A. F., Brena, B., González-Sapienza, G. & Puschner, B. 2013 Microcystins in potable surface waters: toxic effects and removal strategies. *Journal of Applied Toxicology* **34** (5), 441–457.

Wang, H., Ho, L., Lewis, D. M., Brookes, J. D. & Newcombe, G. 2007 Discriminating and assessing adsorption and biodegradation removal mechanisms during granular activated carbon filtration of microcystin toxins. *Water Research* **41** (18), 4262–4270. https://doi.org/10.1016/j.watres.2007.05.057.

Watson, S. B., Monis, P., Baker, P. & Giglio, S. 2016 Biochemistry and genetics of taste- and odor-producing cyanobacteria. *Harmful Algae* **54**, 112–127. https://doi.org/10.1016/j.hal.2015.11.008.

Westrick, J. A., Szlag, D. C., Southwell, B. J. & Sinclair, J. 2010 A review of cyanobacteria and cyanotoxins removal/inactivation in drinking water treatment. *Analytical and Bioanalytical Chemistry* **397** (5), 1705–1714.