Water treatment options for dissolved cyanotoxins

Gayle Newcombe and Brenton Nicholson

ABSTRACT

When treating water subject to a cyanobacterial bloom the first priority should be removal of intact cells using separation techniques such as coagulation or membrane filtration. Chlorination and ozonation are effective for the destruction of residual dissolved microcystins and cylindrospermopsin. Anatoxin-a can be effectively removed using ozone, although chlorine is relatively ineffective. Oxidation techniques do not appear to be the best method for the treatment of saxitoxins under normal treatment plant operating conditions. Powdered activated carbon can be effective for the removal of all toxins, except, perhaps, microcystin LA, provided the appropriate carbon and the correct dose is applied. Granular activated carbon filters show a limited lifetime for the adsorption of most microcontaminants, including cyanotoxins. The biodegradation of cyanotoxins across GAC filters shows great potential as a treatment process.

Key words | algal toxins, cyanobacteria, water treatment

Gayle Newcombe (corresponding author)
Brenton Nicholson
Australian Water Quality Centre,
a partner in the CRC for Water Quality and Treatment,
PMB 3,
Salisbury,
South Australia 5108,
Australia
E-mail: *gayle.newcombe@sawater.sa.gov.au*

INTRODUCTION

Toxic cyanobacteria (blue-green algae) have now been reported in 27 countries and are found on all continents, including Antarctica. Drinking water authorities worldwide are faced with the challenge of treating contaminated water, or the possibility of a toxic bloom occurring sometime in the future.

Approximately 50–95% of the toxic compounds produced by cyanobacteria are bound within the cell, and can be efficiently removed by conventional coagulation/flocculation or membrane treatment, provided the cell wall integrity is maintained (Chow *et al*. 1999; Drikas *et al*. 2001). In all cases there will also be dissolved toxin present, and this issue must be addressed by water authorities challenged by a toxic algal bloom. Knowledge of reliable treatment options, applicable in a range of conditions, for the extracellular toxins produced by cyanobacteria, is of crucial importance to the international water industry. The chemical structures of the most common cyanotoxins are shown in Figures 1–4.

In this paper the authors present an overview of water treatment options for a range of cyanotoxins, based on literature information and the comprehensive experimental programme on cyanobacteria undertaken at the Australian Water Quality Centre.

MATERIALS AND METHODS

Toxin standards

Anatoxin-a was obtained from Calbiochem Corporation (California, USA). Microcystin-LR (m-LR) was obtained from Sapphire Bioscience (Sydney, Australia).

Toxin extracts

Microcystin LR and LA spiking material for ozonation and activated carbon studies was extracted and purified from a local toxic bloom of *Microcystis aeruginosa* in Adelaide, Australia (Newcombe 2002). For the chlorination work, live cells were used, or the material was used after freeze-drying. Saxitoxin spiking material was purified from a toxic scum of *Anabaena circinalis* from Victoria,

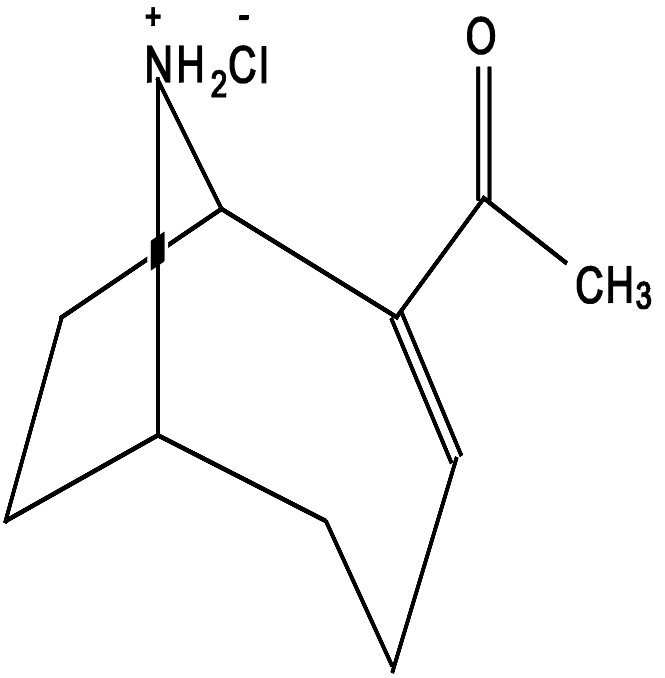


Figure 1 | Anatoxin-a.

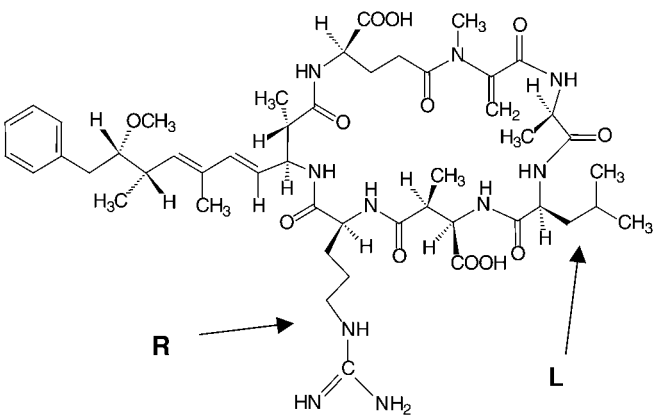


Figure 2 | Microcystin LR, the most common of the 60 microcystin variants identified so far. The two amino acids indicated are leucine (L) and arginine (R). The different microcystins contain various amino groups in these two positions and/or minor changes in other amino acids.

Australia. This material had a toxin profile characteristic of Australian strains of *A. circinalis* (Velzeboer *et al.* 2000); that is, C1 and C2 toxins predominated with lesser quantities of GTX2, GTX3 and saxitoxin (STX). Details are given by Newcombe (2002).

Analysis of toxins

Microcystins were analysed by HPLC with photo-diode array (PDA) detection (Rositano 1996) modified from Meriluoto & Eriksson (1988). Anatoxin was determined by GC with electron capture detection following derivatisation according to the method of Stevens & Krieger (1988) or by HPLC with fluorescence detection following derivatisation with NBD-F according to James & Sherlock (1996). Saxitoxins were determined by HPLC with post-column derivatisation and fluorescence detection (Rositano *et al.* 1998) as modified from Oshima (1995). Mouse bioassays were carried out by intraperitoneal injection of 1.0 ml of extract into 20 g mice.

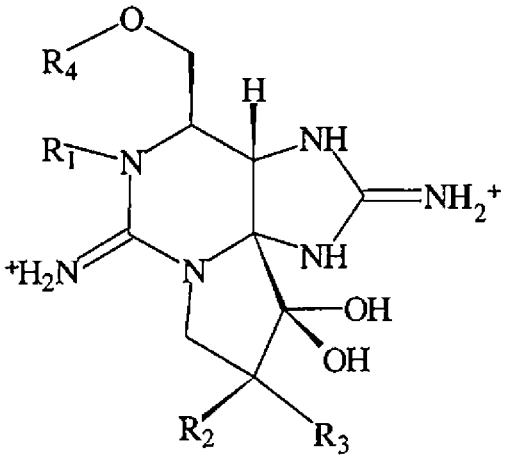
Chlorination

Chlorination experiments were carried out on freeze-dried material containing m-LR and microcystin LA (m-LA), live cells of a culture of *M. aeruginosa* containing mostly m-LR and live cells of a natural bloom of *Nodularia spumigena*. Details are given in Nicholson *et al.* (1994) and Rositano (1996).

Chlorination of saxitoxins was carried out with semi-purified material. Reservoir water was dosed with the semi-purified material, and then with sufficient chlorine to produce a residual of 0.5 mg l^{-1} after 30 min. The pH of samples was adjusted before chlorine dosing and measured after dosing and again after the 30 min contact time. Because of the relatively large chlorine doses required, there were substantial pH changes after the addition of chlorine. The pH at the end of the experiments was taken as the reaction pH and was generally the same as, or very similar to, the pH immediately after chlorine addition. Initial toxin concentrations ranged from approximately 150 μg l^{-1} for C2 through to 10 μg l^{-1} for saxitoxin (Nicholson *et al.* 2003).

Ozonation

Ozone stock solution was added to 250 ml of test solution and allowed to react for 5 min. Residual ozone was purged



	R1	R2	R3	Net Charge	Rel. toxicity
R4=$CONH_2$ (carbamate toxins)					
STX	H	H	H	+2	1
GTX2	H	H	OSO_3^-	+1	0.359
GTX3	H	OSO_3^-	H	+1	0.638
GTX4	OH	OSO_3^-	H	+1	0.726
R4=$CONHSO_3^-$ (n-sulfocarbamoyl (sulfamate) toxins)					
C1	H	H	OSO_3^-	0	0.006
C2	H	OSO_3^-	H	0	0.096

Figure 3 | Saxitoxin class of cyanotoxins. Rel. toxicity indicates the toxicity relative to the most toxic analogue saxitoxin (STX).

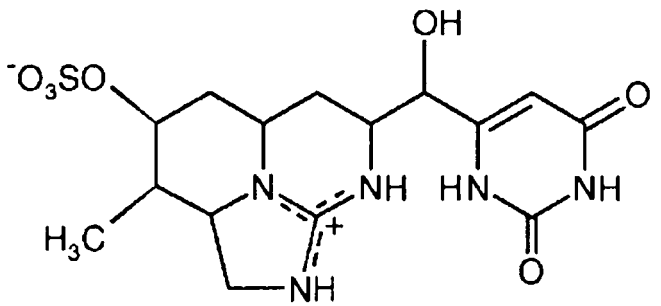


Figure 4 | Cylindrospermopsin

using nitrogen. Full details are given in Rositano *et al.* (2001).

Powdered and granular activated carbon application

Equilibrium and kinetic experiments using powdered activated carbon (PAC) were undertaken as described elsewhere (Cook *et al.* 2001). Granular activated carbon (GAC) pilot and laboratory studies are described by Newcombe (2002).

RESULTS AND DISCUSSION

Chlorination

Hepatotoxins

Microcystins in an extract of freeze-dried material were rapidly destroyed by chlorine; the destruction of toxins correlated well with loss of toxicity as determined by mouse bioassay (Table 1). Based on the reported acute toxicities of microcystins LR and LA (50 $\mu g\,kg^{-1}$) (Rinehart *et al.* 1994), a lethal dose would be around 1 μg per mouse for a 1 ml injection, which agrees well with the analytical results. Results for individual toxins were the same, total toxin concentration is given in Table 1.

Table 1 | Microcystin concentrations and mouse bioassay results after chlorination of an extract of toxic *M. aeruginosa* with aqueous chlorine. Contact time=30 min

Chlorine dose ($mg\,l^{-1}$)	Toxin concentration determined by HPLC ($\mu g\,l^{-1}$)	Microcystin dose injected (μg)	Mouse bioassay result
0	192	3.8	+
0.2	174	3.5	+
0.5	164	3.3	+
0.8	154	3.1	+
1.0	4	0.08	−
2.0	4	0.08	−

+=acutely toxic; −=non-toxic.

The removal of toxins by chlorine was found to be very dependent on pH. The destruction of microcystin

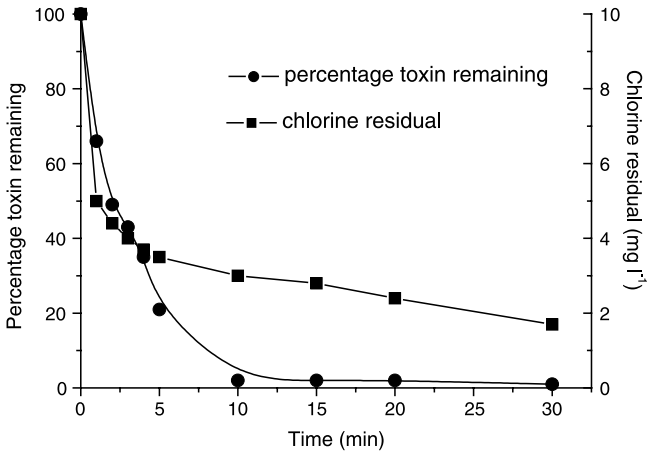


Figure 5 | Percentage toxin remaining, and chlorine residual vs. time for a culture of *M. aeruginosa*.

decreased markedly at pH above 8 for sodium and calcium hypochlorite and above pH 9 for gaseous chlorine. This behaviour reflects the effect of pH on the oxidising potential of hypochlorous acid. Under alkaline conditions (pH>8) chlorine is present predominantly as the hypochlorite ion which is a weaker oxidant than hypochlorous acid, the main species present under neutral to acid conditions.

Chlorine was also found to be effective in destroying toxins present in live cells of both *M. aeruginosa* and *N. spumigena* (Nicholson *et al*. 1994; Rositano 1996). Presumably chlorine is effective at rapidly lysing the cells, thereby releasing the toxins where they react rapidly with chlorine. Figure 5 shows the results with a culture of *M. aeruginosa* where a 10 mg l^{-1} dose of chlorine reduced the concentration of microcystins from 46 to <1 μg l^{-1} (98% removal) in 30 min.

With live cells of *N. spumigena* collected from a bloom, nodularin was reduced from a concentration of 440 μg l^{-1} to <1 μg l^{-1} in 30 min. At this time the chlorine residual was 0.5 mg l^{-1}. On the basis of these and other results, it was concluded that chlorine treatment of cyanobacteria was effective in destroying hepatotoxins such as microcystins and nodularin as long as a free chlorine residual of at least 0.5 mg l^{-1} was present after 30 min and the pH was less than 8. For toxin removal to be effective, it is important that the chlorine demand of the water is satisfied. In waters with a relatively high demand, removal is slower than with pure toxins in high purity water because of the competitive reactions with the natural organic material.

The effective destruction of hepatotoxins by chlorine is contrary to earlier results reported in the literature (Hoffmann 1976; Keijola *et al.* 1988; Himberg *et al*. 1989). Hoffmann (1976) reported no removal of toxicity, determined by mouse bioassay, as a function of chlorine dose. It can now be concluded, based on the more recent determination of acute toxicity of microcystins, that insufficient chlorine was used in these experiments. In the work reported by Keijola *et al.* (1988) and Himberg *et al*. (1989), where toxin removal was determined by HPLC, the low chlorine doses utilised were probably consumed by the naturally occurring organic material and were therefore insufficient to destroy the microcystins present.

Anatoxin-a

Chlorine was found to be relatively ineffective in oxidising anatoxin-a. Anatoxin-a was dosed in to reservoir water at a concentration of 20 μg l^{-1} and treated with varying doses of chlorine. In all experiments the pH was between 6 and 7. At the highest chlorine dose (15 mg l^{-1}), after 30 min contact time the free chlorine residual was 4.5 mg l^{-1} but toxin removal was only 16%. Similar results have been reported previously (Keijola *et al.* 1988; Carlile 1994; Hart *et al*. 1997).

Saxitoxins

Destruction of saxitoxins by chlorine was dependent on both pH and the particular toxin (Figure 6). The form of the chlorinating agent was unimportant when the pH was taken into account. The order of ease of removal of the saxitoxins was STX>GTX3~C2>C1>GTX2. A high removal was possible at pH 9 provided a residual of 0.5 mg l^{-1} free chlorine was present after 30 min contact time (Nicholson *et al.* 2003). Removal as a function of pH was not linear; the degree of removal increased rapidly at around pH 7.5. The more effective removal at higher pH was unexpected as chlorine is known to be a weaker

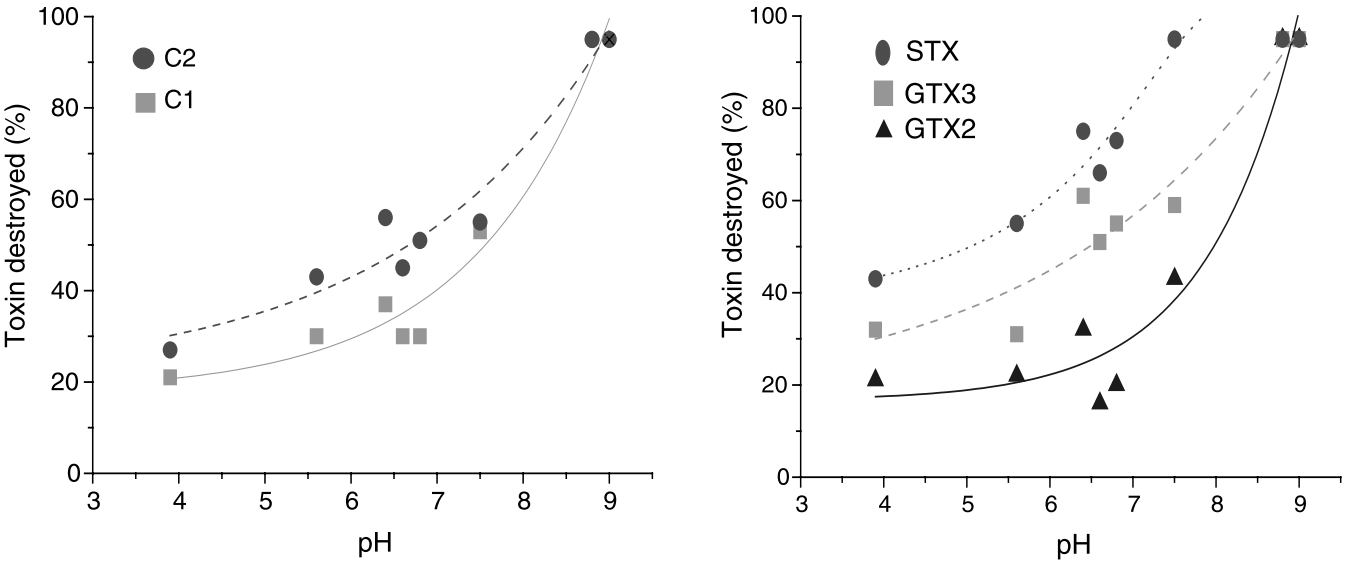


Figure 6 | Percentage saxitoxin destroyed by chlorine as a function of pH. Chlorine dose was sufficient to provide a 0.5 mg l^{-1} residual after 30 min.

oxidant under these conditions. However the more effective removal may be because the toxin molecule was present in an unprotonated form at higher pH and therefore more susceptible to oxidation. This is supported by the fact that, in the detection of saxitoxins using post-column oxidation, sensitivity, which depends on the oxidation of these toxins to fluorescent derivatives, increases as the pH increases from 6.5 (Sullivan *et al.* 1985). Thus oxidation, at least to form fluorescent derivatives, is more efficient as the pH increases.

The feasibility of using chlorine to remove saxitoxins will depend on the pH of the water, the chlorine dose, initial concentrations of toxins and the degree of removal required. Removal may be improved by pH adjustment. Although saxitoxins are not detected by chemical analysis after chlorination under optimum conditions, there is no indication of the nature of the oxidation products. However, toxicity as measured by mouse bioassay is destroyed.

Cylindrospermopsin

Cylindrospermopsin, like the microcystins, is very susceptible to oxidation by chlorine. Oxidation is very rapid with >99% removal in the pH range 6–9 under conditions where a chlorine residual of 0.5 mg l^{-1} is achieved (Senogles *et al.* 2000; Aldridge *et al.* 2001).

Recommendations

Chlorination is an effective, simple method for the destruction of microcystins and cylindrospermopsin. At the moderate water temperatures studied so far, the doses of chlorine required to maintain a residual in the distribution system would be expected to result in toxin-free water. However, it is well known that the reaction with natural organic material in water to form disinfection by-products is strongly dependent on temperature, and it is possible that at lower temperatures the rate of reaction with cyanotoxins would be greatly reduced. This aspect of the application of chlorine requires further research. The oxidation of saxitoxins by chlorine is effective only at high pH (>8–9). Therefore pH control must be applied for the utilisation of this method for removal of the saxitoxin class of cyanotoxins. Chlorination would not be recommended as a method for the detoxification of drinking water containing anatoxin-a.

Ozonation

Ozone is an effective oxidant when used in water treatment; however it should be noted that the chemistry of ozonation is complex and the most effective oxidation reactions are through the hydroxyl radical pathway. Hydroxyl radicals are formed on reaction of the molecular ozone with natural organic material present in water. Higher pH is favourable for radical production, as is low alkalinity. In addition, natural organic matter consumes ozone radicals, and competes with the target compound such as algal toxins for the stronger oxidant. This effect is described for the odour compounds MIB and geosmin in Ho *et al.* (2002). As a result the ozonation of algal toxins, or any microcontaminant, is dependent on a range of water quality parameters, and prediction of the combined effects is not always possible.

Microcystins

Ozonation of microcystins LR and LA (m-LR and m-LA) was undertaken in a batch reactor in two treated waters (conventional treatment, prior to chlorination) of different water quality. Hope Valley has a dissolved organic carbon concentration of 5 mg l^{-1} and Edenhope 19 mg l^{-1}. There was a strong effect of water quality which was related to the ozone demand of the water. In both waters the microcystins were destroyed to below detection at an ozone dose sufficient to retain a residual of molecular ozone for 5 min (Figure 7).

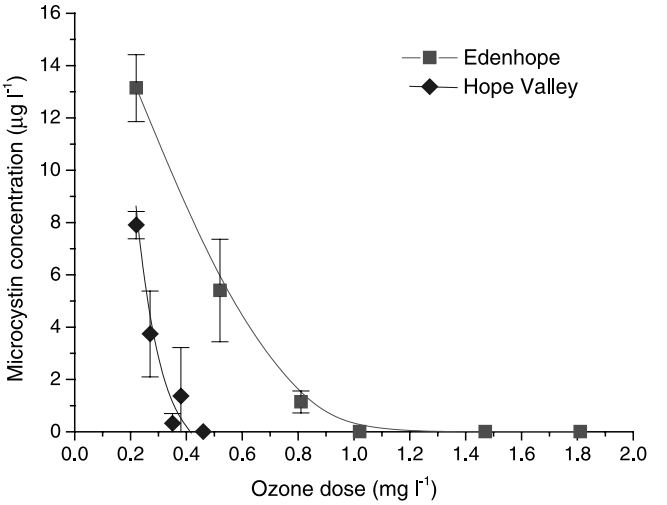


Figure 7 | Microcystin concentration as a function of ozone dose in two treated waters.

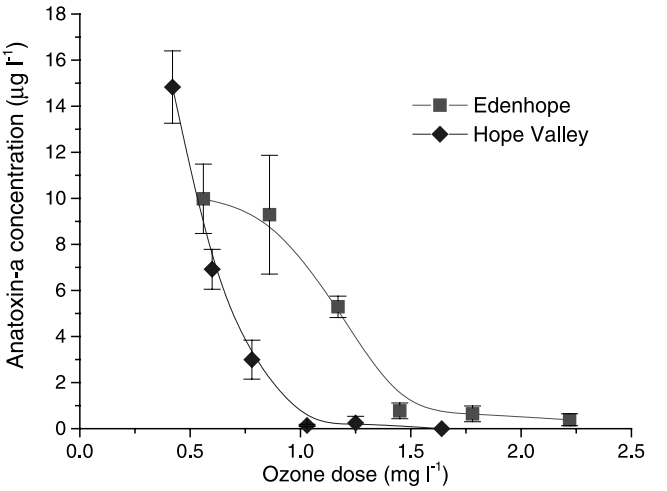


Figure 8 | Anatoxin-a concentration as a function of ozone dose in four treated waters.

Anatoxin-a

Results for anatoxin-a were similar to those obtained for microcystins (above), with slightly higher ozone residuals required for destruction to below detection (Figure 8).

Saxitoxins

A mixture of saxitoxins was exposed to ozone under the same conditions as described above. In this case, all of the toxins appear to be fairly resistant to oxidation by ozone (Figure 9).

Cylindrospermopsin

Aldridge *et al.* (2001) reported effective degradation of cylindrospermopsin using ozone in laboratory trials. The conditions of the experiment were unclear, as the toxin spiking solution was only semi-purified, and added significantly to the ozone demand of the water. However, the authors reported that the reaction required low contact times, and doses of ozone that were below the demand of the water. Given the ready destruction of cylindrospermopsin by chlorine, its degradation by ozone, which is a stronger oxidant, is not unexpected.

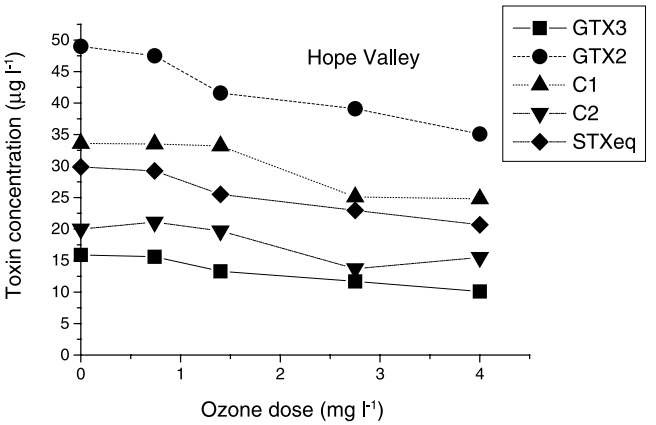


Figure 9 | Saxitoxin concentration as a function of ozone dose in Hope Valley treated water.

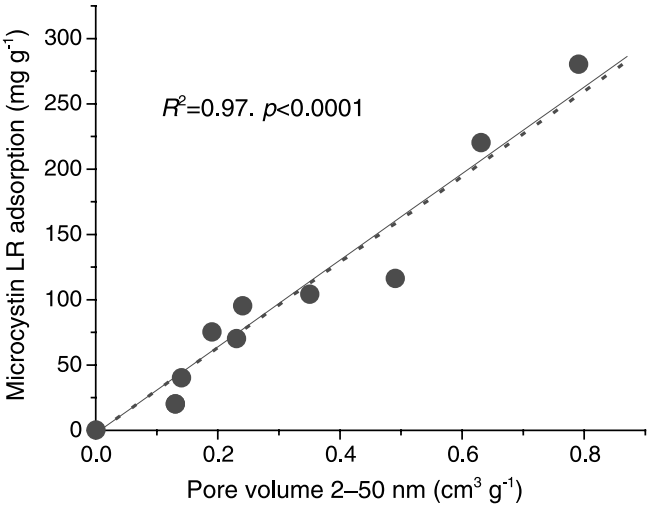


Figure 10 | Microcystin LR adsorption vs. pore volume of activated carbons.

Recommendations

At moderate temperatures (>16°C) ozone is effective for the destruction of microcystins and anatoxin-a under the conditions of dose and contact time usually employed for the deactivation of *Cryptosporidium* and *Giardia*. An ozone dose insufficient to retain a residual for longer than 1 minute should not be relied upon for the destruction of the toxins. There is anecdotal evidence that microcystin is not destroyed under such conditions at low temperatures. This aspect of the ozonation of toxins requires further study, as microcystins are found in a wide range of climates. Saxitoxins would not be destroyed completely under the conditions suggested for anatoxin-a and microcystins. Cylindrospermopsin appears to be susceptible to ozonation, probably because of the double bond in its structure. However, further work is required to determine the effect of water quality conditions and ozone CT values (concentration × time) required in a range of waters.

Powdered activated carbon

Microcystins

The information available in the literature on the adsorption of m-LR on to activated carbon indicates that, as with the adsorption of most microcontaminants, the removal efficiency is dependent on the type of activated carbon and the water quality conditions (Hart & Stott 1993; Donati *et al.* 1994; Lambert *et al.* 1996). Several studies have shown that chemically activated wood-based powdered activated carbons are superior for the adsorption of this toxin (Hart & Stott 1993; Donati *et al.* 1994; Craig & Bailey 1995). Donati *et al.* (1994) related this to the volume of large pores (2–50 nm) in the carbons, appropriate in size for the m-LR molecule (molecular weight 994). Figure 10 shows the relationship between m-LR adsorption at equilibrium, and the volume of pores in the range 2–50 nm. A clear linear relationship is seen, indicating a strong dependence on pore volume, and limited influence of the surface chemistry of the carbons.

Microcystin LR is seldom the only microcystin present in a toxic algal bloom, and in many regions m-LR is not the most commonly occurring variant (Falconer *et al.* 1999). Very little information is available in the literature on the effect of water treatment processes on other variants. The only published investigation of the adsorption of microcystin variants other than m-LR used relatively impure toxin extracts (Mohamed *et al.* 1999). The authors suggested that differences seen in the adsorption of the microcystin variants could have been due to different contaminant levels in the spiking material. The UKWIR undertook a computer modelling study to compare the octanol/water partition coefficients of nine microcystin

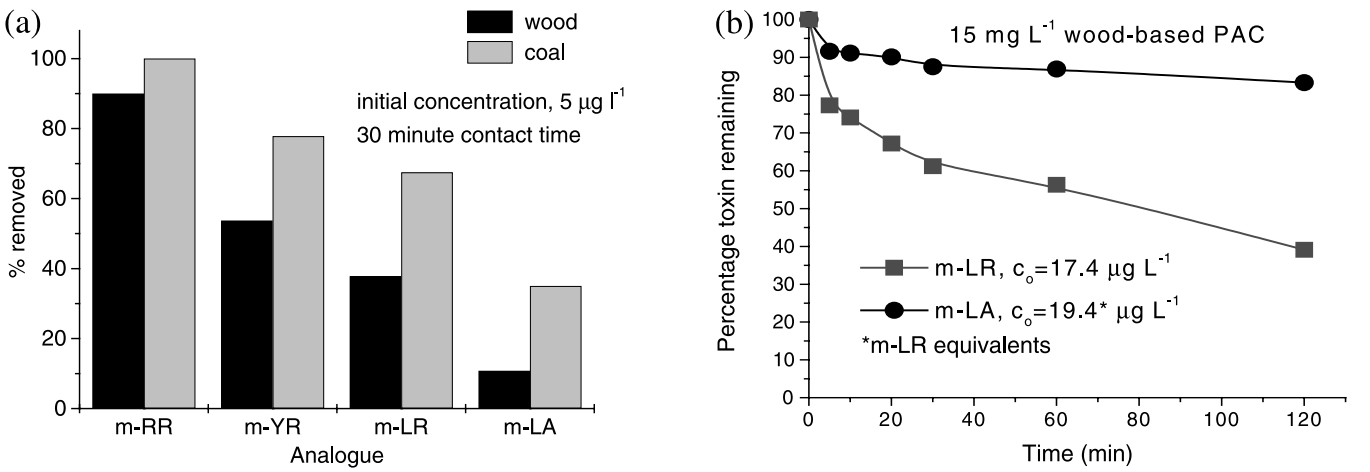


Figure 11 | Adsorption of microcystin variants (a) at 30 minutes contact time, (b) as a function of time.

variants (UKWIR 1997). With this information, and molecular size data, the authors concluded that the variants should respond similarly to water treatment processes and, in particular, that the variants would be adsorbed on to activated carbon to the same, or greater, extent as the commonly studied variant microcystin LR.

Figure 11a shows the large differences observed in the adsorption of four microcystin variants on to two activated carbons. The results are counter-intuitive: the adsorption increases as the hydrophobicity decreases and molecular weight increases, when the opposite trend could be expected. Electrostatic effects are assumed to be the cause of this trend, and these are currently under investigation. Figure 11b displays the large difference in the adsorption of m-LR and m-LA as a function of time. Computer modelling of the kinetics of adsorption was used to predict the PAC doses required to reduce the two compounds to below the WHO guideline of 1.0 $\mu g\ l^{-1}$ in 60 min. The results are given in Table 2. Clearly, the differences in adsorption between microcystin variants will have a significant effect on treatment options available to water suppliers.

Anatoxin-a

Very limited information exists on the adsorption of anatoxins by powdered activated carbon. The removal of anatoxin-a was studied on one activated carbon, a wood-based carbon found to be suitable for m-LR removal (Hart & Stott 1993). As the structure, in particular the size, of the two compounds is very different, it is unlikely that the most suitable carbon would be the same for both compounds. Keijola *et al.* (1988) also investigated the adsorption of anatoxin-a. They observed reasonable removals; however, no details are available on the activated carbon used, or the water quality after spiking with the algal material. There is potential for the method to be successful; however, a systematic study into the effect of activated carbon type, water quality and contact time is required before recommendations can be made.

Table 2 | Predicted PAC doses required to obtain a concentration of 1 $\mu g\ l^{-1}$ after 60 min contact

Inlet concentration ($\mu g\ l^{-1}$)	m-LR PAC dose ($mg\ l^{-1}$)	m-LA PAC dose ($mg\ l^{-1}$)
10	38	⩾100
5	29	95
2	15	50

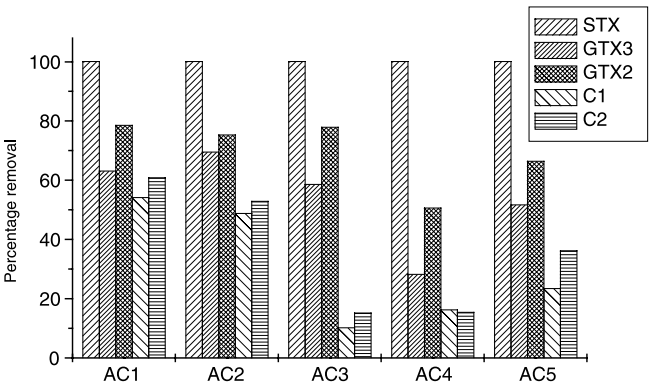


Figure 12 | Percentage removal of saxitoxins for five activated carbons. Contact time=1 h, carbon dose=30 mg l^{-1}.

Saxitoxins

Figure 12 shows the percentage removals from a mixture of saxitoxins by five powdered activated carbons. As a general trend, the adsorption of the compounds decreases as STX>GTX>C toxins. As that is also the order of toxicity of the compounds, PAC is effective for the overall removal of toxicity. Although the charge of the compounds shows a similar trend (STX(+2)> GTX(+1)>C(0)) this is unlikely to be the major effect on adsorption as the carbon with the most positive surface charge (AC2) also displays the highest adsorption. The size of the compounds in solution follows the trend STX<GTX<C toxins and it is likely that the relationship between the size of the compound and the pore volume distribution of the activated carbon plays the major role.

Cylindrospermopsin

There is no information available in the international peer-reviewed literature on the removal of cylindrospermopsin by PAC. Bailey *et al*. (1999) reported good removals with a wood-based PAC at doses below 30 mg l^{-1}, and contact time of 30 min, and Cullen (2001, personal communication) obtained a maximum of 60% removal for a range of activated carbons at doses around 6 mg l^{-1}. Aldridge *et al*. (2001) reported 50% removal of the toxin with a dose of only 2.7 mg l^{-1} when the initial concentration was approximately 2.5 μg l^{-1}. No details were given regarding the contact time or type of activated carbon. As with anatoxin-a, a systematic study of the adsorption of this toxin is required.

Granular activated carbon

Microcystins

Figure 13a shows the results of spiking m-LA during a granular activated carbon pilot plant trial. The pilot GAC

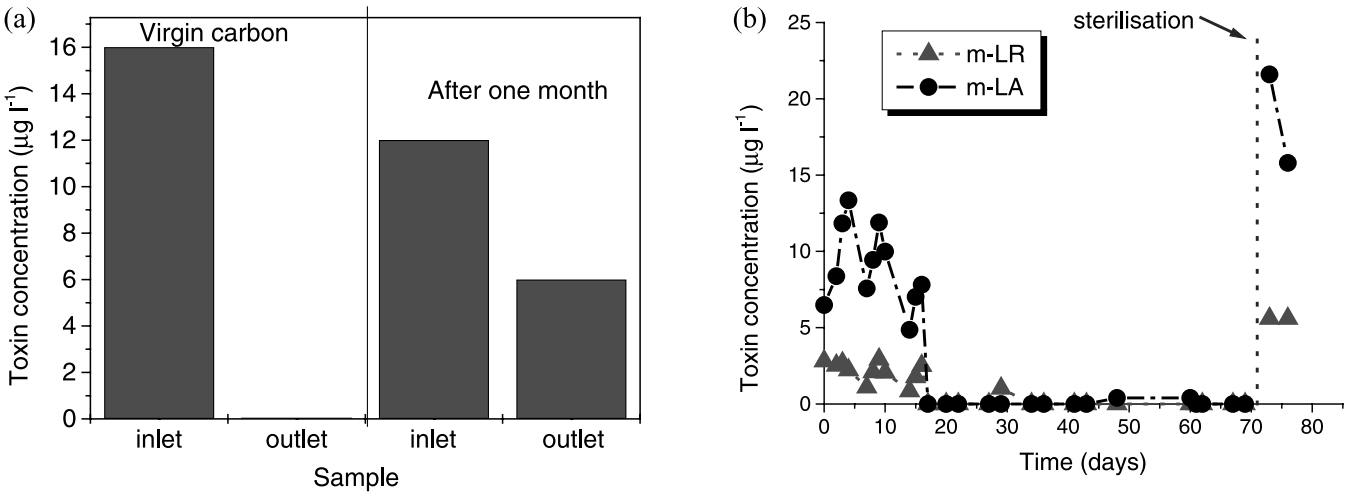


Figure 13 | Microcystin removal across GAC filters, adsorption and biodegradation.

filter was fed with treated water prior to chlorination. At intervals, the GAC filter feed water was spiked with a mixture of m-LR and m-LA. In Figure 13a the inlet and outlet m-LA concentrations at the start of the trial and after 1 month of running the filters are shown. As illustrated, there is already breakthrough of m-LA above acceptable limits after 1 month. Microcystin LR also broke through, but at a lower level. This can be attributed to the level of DOC in the water (5 mg l^{-1}), providing competition for adsorption sites and reducing the adsorption of the toxins. After the 6 months of the pilot trial, a sample of GAC was taken from the filter and used in a laboratory scale GAC filter, where the toxins could be dosed for a longer period. Figure 13b shows the removal of m-LR and m-LA across the lab-scale GAC filter over a 68 day period. The inlet concentration was maintained at approximately 20 μg l^{-1} of each toxin. As expected, initially both toxins were detected in the outlet water. However, after 16 days the removal mechanism clearly shifted from adsorption to biodegradation, with both toxins removed to below detection. After 68 days the carbon was removed, and sterilised by drying using rotary evaporation at 40°C. The inlet concentration was increased to around 30 μg l^{-1} of each toxin. The removal prior to sterilisation was clearly biodegradation, as the sterilisation procedure resulted in significant toxin breakthrough.

The biodegradation of m-LR is well established. Jones & Orr (1994) reported the rapid biodegradation of m-LR after the treatment of a toxic bloom of *Microcystis aeruginosa* with an algicide. However, the biodegradation only occurred after a lag phase of several days. The authors suggested the initial period was required for the microorganisms to acclimatise to the toxin as a food source. This lag phase in microcystin biodegradation has been reported by a number of authors (Lam *et al.* 1995; Cousins *et al.* 1996). The UKWIR have reported significant biodegradation of m-LR on GAC filters (Carlile 1994; UKWIR 1996). In waters with a prior history of blooms, microcystins and nodularin have been reported to be readily removed without a lag phase, suggesting that the microorganisms necessary for degradation are already present in sufficient numbers (Rapala *et al.* 1994; Heresztyn & Nicholson 1997).

Anatoxin-a

GAC appears to be effective for the removal of anatoxin-a for a period of time (Carlile 1994; UKWIR 1996; Bailey *et al*. 1999). Carlile (1994) used small-scale column tests to model full scale GAC bed life, and predicted breakthrough after around 15 weeks. This could be expected to be prolonged by biodegradation within the GAC filter, as was reported with slow sand filtration of anatoxin-a (Keijola *et al*. 1988). The information currently available does not allow the confident recommendation of GAC filtration for this toxin.

Cylindrospermopsin

No data available.

Saxitoxins

During a 6 month laboratory scale GAC trial using a coconut-based carbon, a mixture of saxitoxins was spiked into the inlet water three times: initially, after one month and after 6 months. The trends in removal of the individual toxins were the same as those illustrated in Figure 12. After 6 months the removal of toxicity, measured in saxitoxin equivalents, was still satisfactory: approximately 70% (Newcombe 2002).

Recommendations

In general, mesoporous carbons, that is, carbons with a large number of large pores, are the best for the removal of microcystins. Chemically activated wood-based carbons are often highly mesoporous, although recently a coal-based carbon has shown superior adsorption properties (Figure 11). If several variants of microcystin are present, which is most frequently the case, assessment of activated carbon should not be based on the adsorption of m-LR alone. It appears that m-RR is very readily removed, whereas activated carbon adsorption should not be relied upon for the removal of m-LA. PAC dose requirements for microcystin removal at a particular water treatment plant can be predicted using adsorption models. From this information, water authorities can make an informed choice

regarding water treatment options. GAC lifetime for the removal of microcystins would be limited under most conditions in the absence of biodegradation. More research is required regarding the potential for utilising biodegradation of microcystins under a range of water quality conditions. Although the limited information available suggests anatoxin-a and cylindrospermopsin could be removed using activated carbon, a systematic study of a range of carbons and a range of waters is required prior to confident application of the adsorbent. There also appears to be potential for the use of biodegradation for anatoxin-a and cylindrospermopsin; the requirements for further research are the same as for microcystins.

Both PAC and GAC are effective for the removal of saxitoxins, primarily because of the effective removal of the most toxic of the analogues, STX and GTX toxins. Microporous carbons (with pores <2 nm) such as good quality coal and coconut carbons, are recommended.

Other treatment methods

UV photolysis has been found to be effective for the destruction of some toxins; however, the conditions required are often outside the range of practical water treatment application. For example, Carlile (1994) studied the UV irradiation of anatoxin-a at 254 nm and found reasonable removal of toxin at doses two orders of magnitude higher than those usually utilised for disinfection. In the same study the author found that m-LR was more readily destroyed than anatoxin-a. Cylindrospermopsin was found to degrade rapidly in sunlight in the presence of algal extract, while in its pure form, in the absence of other organic material, the toxin did not degrade (Chiswell *et al.* 1999). This effect was also seen with m-LR in the presence and absence of organic material (Rositano 1996). Titanium dioxide has been used successfully as a catalyst for the destruction of m-LR and cylindrospermopsin by UV photolysis (Lawton *et al.* 1999; Feitz *et al.* 1999; Cornish *et al*. 2000; Senogles *et al.* 2001; Shephard *et al.* 2002). Although not currently accepted as a drinking water treatment process, this technique may be viable at some future stage.

CONCLUSIONS

When treating water subject to a cyanobacterial bloom the first priority should be removal of intact cells using separation techniques such as coagulation or membrane filtration. Residual dissolved toxins can be treated using oxidation techniques and/or powdered/granular activated carbon. Chlorination and ozonation are effective for the destruction of microcystins and cylindrospermopsin at moderate water temperatures. Presently, little information is available regarding the effect of temperature on these oxidation processes, and the efficacy of these treatments should be investigated under the range of temperatures and oxidant doses used at the water treatment plant affected. Anatoxin-a can be effectively removed using ozone, although chlorine is relatively ineffective. Oxidation techniques do not appear to be the best method for the treatment of saxitoxins under normal treatment plant operating conditions. Powdered activated carbon can be effective for the removal of all toxins, except, perhaps, m-LA, provided the appropriate carbon and the correct dose is applied. However, under conditions of high toxin concentration over a prolonged period this option may become prohibitively expensive. Microcystin variants show a significant range of adsorbabilities and that should be taken into account when activated carbon application is considered. Granular activated carbon filters show a limited lifetime for the adsorption of most microcontaminants, including cyanotoxins. However, the biodegradation of cyanotoxins across GAC filters shows great potential as a treatment process, particularly if the optimum conditions for biodegradation can be identified, and perhaps imposed on the filter.

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