Toxic Cyanobacteria in Water: A guide to their public health consequences, monitoring and management
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Chapter 9. REMEDIAL MEASURES

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The management and control of cyanobacteria in water supply storage facilities and of cyanotoxins in drinking water may be approached at a number of points and levels in the hierarchy of the total supply system. A detailed assessment of water supply systems with respect to the potential impact of blooms and cyanotoxins on water quality and public health has been presented in Chapter 6. The first preference for control is the prevention of eutrophication, which is discussed in Chapter 8. The next level of management response is reservoir and water body management which can include some engineering techniques to alter hydrophysical conditions in the water body in order to reduce cyanobacterial growth (section 8.5). The more immediate and short-term control techniques which can be used in the management of raw water abstraction include the avoidance of contamination by positioning of offtakes, selection of intake depth, offtake by bank filtration, and the use of barriers to restrict scum movement. Another intervention technique is chemical treatment with algicides. Algaecides have been, and will continue to be, used as emergency measures for the control of cyanobacteria, and their role in management strategies needs to be assessed from practical and environmental viewpoints. The final option for management of cyanobacterial problems and cyanotoxins in water supplies is within the treatment system. Research on removal of algal and cyanobacterial cells has been widely published (see review by Mouchet and Bonnélye, 1998) and recent work has generated quite detailed knowledge on cyanotoxin removal during drinking water treatment.

Much of the work on cyanotoxin removal has focused on single treatment steps, and a few studies have investigated the common combinations of coagulation, clarification and filtration. As a research approach, this is useful because assessments of the performance of individual treatment steps may be generalised more readily than observations gained in complete, but individual, supply systems with their respective site-specific characteristics. However, management approaches aimed at providing safe drinking water from cyanobacteria-infested surface waters require considering the system as a whole, and using different combinations of resource management tailored to the specific locality and different treatment steps. In such an overall approach, steps that individually may be unsatisfactory can have their place in combination with others and thus contribute to a multi-barrier approach. Furthermore, the individual aspects of each drinking water supply necessitate local assessment of performance as well as local optimisation of resource management and treatment strategies.

9.1 Management of abstraction

Management of raw water abstraction is effective in reducing the amount of cyanobacteria in the raw water, often by orders of magnitude. This can be achieved by choosing an optimum position for the offtake, or by abstracting surface water through bank filtration.

9.1.1 Direct abstraction from surface water bodies

General resource management, including hydraulic intervention measures, are described in Chapter 8. The horizontal and vertical distribution of cyanobacterial populations can vary enormously throughout a water body, whether in a lake, reservoir or river. This has obvious implications for both the siting of offtakes and the choice of offtake depth. Considerable contamination of raw water can be avoided by locating offtakes away from sheltered bays where scums may accumulate (usually downwind of the prevailing winds during the critical summer growth period). If this is not practical, it may be possible to employ temporary extensions to pipe intake points.

Selection of offtake depth can also be important in reducing contamination by avoiding surface or subsurface maxima of cell numbers. Many modern reservoir offtake structures (towers) have the provision for multiple offtake depths. If multiple offtakes are not available it may be possible to install siphon offtakes, at least as a temporary measure in small systems. In relation to cyanobacterial contamination, the choice of intake depth must take into account the time of daily maximum surface accumulation of cells and the amplitude of passive diurnal vertical sinking and rising of cells due to light-and photosynthetic-driven changes in cell buoyancy. In thermally stratified, mesotrophic reservoirs, attention must be given to the possibility of meta-limnetic maxima (i.e. maxima between warm upper and cold, lower water layers) of *Planktothrix rubescens* (syn. *Oscillatoria rubescens*).

Operators need to become familiar with the amplitude of vertical movement of cyanobacterial populations, and also with the potential for the formation of metalimnetic peaks, in order to avoid high cell densities as much as possible. This requires multiple depth sampling to determine vertical profiles of cyanobacterial cell density. Collecting information and building up knowledge and understanding of local ecology and conditions can increase flexibility in the management of blooms (see Chapter 10).

Another option to avoid contamination is to employ physical barriers or booms at the surface to prevent surface scums accumulating near the offtake site. Surface booms or curtains, similar to oil-spill containment booms, have been used successfully in Australia, the UK and North America to keep surface scums away from offtake structures (see Figure 9.1 in the colour plate section). These physical barriers often only extend to a depth of 0.5-1.0 m, and do not affect bulk horizontal flow significantly. This technique is a worthwhile emergency measure for transient blooms and its use will depend upon the practical aspects of installation.

9.1.2 Bank filtration and groundwater recharge

An abstraction method that has proved to be very effective in removing particles and many dissolved compounds in localities with suitable underground conditions is bank

filtration or abstraction of groundwater artificially recharged with surface water. The process uses bore holes or infiltration galleries which are located near to the banks of a surface water supply (river or reservoir). These wells fill with water which has infiltrated through the intervening porous soil materials. Depending upon the underground characteristics, water may travel for several hours, or even for weeks before it reaches the well. Longer retention times may enhance purification, but even retention times of between a few hours and days have substantially improved water quality. Many types of soils may be suitable, provided they allow water flow, are not too coarsely structured to achieve a filtering effect, or are not in contact with saline or otherwise unsuitable groundwater. Planning bank filtration requires local assessment of sites for their suitability.

Evaluation of bank filtration with respect to cyanotoxin removal is currently only beginning, and no published results are available. A study of elimination of algal and cyanobacterial taste and odour compounds has shown very effective removal by bank filtration at three study sites (Chorus *et al.,* 1993). Because of the generally positive experience with respect to removal of suspended materials, micro-organisms and a variety of chemical contaminants (Laszlo, 1984; UNDP/WHO, 1992) it may be expected that bank filtration will be a highly promising abstraction method to avoid contamination with cyanobacterial cells as well as dissolved toxins. This expectation is supported by the favourable results of a laboratory study from Finland which demonstrated good performance of experimental soil and sediment columns for both cell and toxin removal (Lahti *et al.,* 1996). In this case, lake water was inoculated with both toxic and non-toxic cultures of cyanobacterial cells and pure microcystin-LR and filtered through soil and lake sediment columns. It was found that during the experimental period of one week, both cells and dissolved toxins were removed very efficiently, although there was some breakthrough in sediment columns at high loadings. The mean rates of removal for cells were 93.7-99.7 per cent and 97.5-99.5 per cent for extracellular toxins for both soil and sediment columns. It was suggested that the removal of microcystins in this filtration process was the result of both adsorption and biodegradation (Lahti *et al.,* 1996). However, the relative performance of the two processes would be very site specific and dependent upon local soil characteristics and microbial activity.

The performance of bank filtration in relation to adsorption capacity, overloading and the potential for release over time of toxins from trapped cells would require monitoring (see Chapter 13 for methods).

9.2 Use of algicides

Algaecides are used in reservoirs to control cyanobacterial growth and to prevent or reduce to some extent the problems of toxins in the associated drinking water supply. Their role in the management scheme may be to provide effective short-term control of growth of cyanobacteria, at one point in time, particularly in circumstances where alternative drinking water sources are not available and preventive measures (as outlined in Chapter 8) are not feasible or not yet effective. Algicide treatment has been proposed as being more cost-effective than toxin removal in drinking water treatment plants, as has been suggested for the control of off-flavour problems (McGuire and Gaston, 1988), because an extended period of persistent blooms greatly enhances the need for additional treatment for toxin removal. However, experience with abatement of off-flavours caused by cyanobacteria through algicide treatment has also demonstrated

that this treatment may actually enhance the problem by supporting the development of species resistant to the treatment (Izaguirre, 1992).

Environmental concerns have been raised because the most commonly used algicide, copper sulphate, has broad ecological impact. It should be used only in dedicated water supply reservoirs in special circumstances, but is nevertheless an unsatisfactory long-term solution. In many countries, national or local environmental regulations prohibit or limit the use of algicides due to their adverse environmental impact. This needs to be established prior to considering the use of algicides.

Algicides, like all management techniques, must be applied correctly to work effectively. If algicides are used they must be applied at the early stages of bloom development when cell densities are low, in order to reduce the potential for liberation of the high concentrations of intracellular toxin that may be associated with dense blooms. Early application will further enhance the effectiveness of treatment because cyanobacterial cells can form a major part of the "copper demand" along with other organic matter in natural water.

A major limitation of any agent which disrupts cyanobacterial cells is the release of toxins and of taste and odour compounds from the cells. A range of studies have indicated that cyanotoxins are predominantly intracellular in healthy cells, and are only released into the water at an advanced stage of bloom senescence, or following treatment with chemicals such as algicides (Lahti *et al.,* 1996). This release can be quite rapid and has been shown to occur within 3-24 hours in different studies (Jones and Orr, 1994; Kenefick *et al.,* 1993). These dissolved toxins will then disperse and be diluted throughout the water body, but will not be removed by conventional flocculation and filtration procedures. Installation of additional treatment for removing cyanotoxins may be costly. The dangers of treating dense blooms with algicides was demonstrated in an incident which occurred on tropical Palm Island, Australia, where members of the community became ill with hepato-enteritis following treatment of the water supply reservoir with copper sulphate for a cyanobacterial bloom problem (Bourke *et al.,* 1983) (see Box 4.3).

If algicides are used to control toxic cyanobacteria, the reservoir should be isolated for a period to allow the toxins and odours to degrade (see section 3.4). Unfortunately, very little data exist on the withholding period in relation to toxin loss, but it could be in excess of 14 days (Jones and Orr, 1994).

In some cases algicide treatment may be unsuccessful or only partially successful. This can be due to inadequate dispersal and contact with the target organisms, variable sensitivity of cyanobacteria, and reduced toxicity due to complexation of the copper (Burch *et al.,* 1998). The form of copper most toxic to aquatic organisms is the free cupric ion (Cu^{2+}) and this can be reduced by complexation with both inorganic ligands under alkaline conditions, and organic ligands present in natural waters (McKnight *et al.,* 1983).

9.2.1 Copper sulphate

Chemical control of algae in water supply storage has been a widespread water quality management practice for over 100 years. Records of the use of copper sulphate date

from 1890 in Europe (Sawyer, 1962), from 1904 in the USA (Moore and Kellerman, 1905), and at least since the mid 1940s in Australia (Burch *et al.,* 1998). Copper sulphate has been regarded as the algicide of choice because it is economical, effective, relatively safe and easy to apply. It is also considered to be of limited significance to human health at the doses commonly used (WHO, 1996) and has been considered not to cause extensive environmental damage (McKnight *et al.,* 1983; Elder and Home, 1978). The latter point has been an issue of debate for some time (see Mackenthun and Cooley, 1952) because copper tends to accumulate in lake sediments (Sanchez and Lee, 1978; Hanson and Stefan, 1984). In some cases it appears not to be remobilised and is bound permanently to the bottom sediments (Elder and Home, 1978; Sanchez and Lee, 1978). However, in a study of 10 drinking water dugouts (small reservoirs) in Canada, sediment copper (previously accumulated from copper sulphate treatments) was released back into the open water under low dissolved oxygen conditions in the hypolimnion in summer (Prepas and Murphy, 1988). It has also been suggested that sediment-bound copper could have an impact on the benthic macroinvertebrate community (Hanson and Stefan, 1984). It is important to remember that copper and other heavy metals differ from some other toxic contaminants in that they are not biodegradable, and once they have entered the environment their potential toxicity is controlled largely by their speciation or physicochemical form (Florence, 1982). Copper sulphate treatment has been shown to cause short-term changes in phytoplankton abundance and species succession (Effler *et al.,* 1980; McKnight, 1981). Fish kills may also occur following copper sulphate treatment, although it is not clear whether this is as a result of copper toxicity or oxygen depletion (Hanson and Stefan, 1984).

A recent extensive survey of water utilities in the USA and Canada indicated that copper sulphate is by far the most widely used algicide, although other alternatives are used under some circumstances (Casitas Municipal Water District, 1987). Some of the compounds that have been used and evaluated for potential as algicides over the years are summarised in Table 9.1.

McKnight *et al.* (1983) give an assessment of the use of copper sulphate for the control of nuisance algae and cyanobacteria. They also indicate that there are wide differences in copper sensitivity among species. The relative growth inhibiting concentrations for a range of phytoplankton are given in terms of cupric ion activity (i.e. $[Cu^{2+}]$), derived from laboratory toxicity studies. The toxic cupric ion activities range from greater than 10^{-6}-10^{-11} M ($0.063\text{-}6.3 \times 10^{-7}$ mg l^{-1} Cu^{2+}) for species of diatoms, dinoflagellates, green algae and cyanobacteria - a difference of over four orders or magnitude (McKnight *et al.,* 1983). These toxic Cu^{2+} concentrations are very much less than the usual doses applied as total copper in copper sulphate treatments. The relative toxicity is given in terms of ionic copper because it is believed that phytoplankton react principally to the concentration of Cu^{2+} or loosely complexed copper rather than the total dissolved metal in the water.

McKnight *et al.* (1983) have used these findings to develop an experimental procedure to determine the required dose rates for target species in individual reservoirs, taking account of the particular water chemistry. This experimental procedure to determine dose rates is suggested as more effective than simple empirical formulae, based on pH and alkalinity, which were not very useful (McKnight *et al.,* 1983). The experimental approach requires access by the water supply operators to a good level of biological and chemical expertise and analytical capacity. The approach is based on first determining the cupric ion activity as a function of added copper, and thereby the complexing

capacity of the reservoir water by a copper ion selective electrode. This is followed by a culture assay to determine the sensitivity of the particular nuisance algae to copper. The local nuisance species preferably need to have been isolated into laboratory culture. The required copper sulphate dose rates can be derived from a simple formula relating growth inhibition, in terms of cupric ion concentration, to the Cu^{2+} concentrations in the reservoir after complexation (McKnight *et al.,* 1983).

Table 9.1 Compounds that have been used as algicides, their formulation and key references

Compound	Formulation	Reference(s)
Copper sulphate	$CuSO_4.5H_2O$	McKnight *et al*., 1983; Holden, 1970; Palmer, 1962; Casitas Municipal Water District, 1987
Cutrine® - plus	Cu alkanolamine. $3H_2O^{++1}$	Humburg *et al.,* 1989
Copper - triethanolamine complex	Cu $N(CH_2CH_2OH)_3.H_2O$	Humburg *et al.,* 1989
Copper citrate	Cu_3 $[(COOCH_2)_2C(OH)COO]_2$	Casitas Municipal Water District, 1987; Raman, 1988; McKnight *et al*., 1983; Fitzgerald and Faust, 1963
Potassium permanganate	$KMnO_4$	Fitzgerald, 1966; Holden, 1970
Chlorine	Cl_2	Holden, 1970

[1] Copper II alkanolamine complex

9.2.2 Copper chelates

The problem of the reduced effectiveness of copper sulphate treatment in hard alkaline water has long been recognised (Palmer, 1962; Casitas Municipal Water District, 1987). Chelated copper algicides were developed to overcome the problems of the complexation and precipitation loss of toxic copper under these circumstances. Examples of copper chelate algicides include copper ethanolamine complexes and copper citrate (Table 9.1). Copper citrate has been used as an algicide in the USA (Casitas Municipal Water District, 1987; Raman, 1988). It is available either as a commercial preparation (Hoffman *et al.,* 1982) or by simultaneously dosing copper sulphate and citric acid (Raman, 1988). It is claimed that the use of citric acid as a chelating agent enhances the solubility of copper allowing it to remain in solution longer under alkaline conditions (Raman, 1985; 1988). Raman (1988) recommends applying copper sulphate: citric acid in the weight ratio 2:1 in high-alkalinity waters (> 40 mg l^{-1} $CaCO_3$). A study which examined equilibrium speciation of copper in water to determine the changes in distribution of Cu(II) in relation to pH, dissolved organic carbon (DOC) and citrate was carried out by Casitas Municipal Water District (1987). This study demonstrated that citrate greatly enhances the solubility of copper even in the presence of appreciable alkalinity (100 mg 1^{-1}). McKnight *et al.* (1983) suggested that the advantage of using synthetic copper chelating agents in hard, alkaline waters probably results from decreasing the supersaturation of malachite ($Cu(OH)_2CO_3$) and tenorite (CuO) and thereby the rate at which equilibrium with these insoluble forms (precipitates) is approached. It is possible that a longer time taken to reach equilibrium would result in the maintenance of toxic ionic Cu^{2+} activities and the inhibition of algal growth for longer

periods after dosing (McKnight *et al.,* 1983). It is acknowledged that, despite their relatively widespread use in the USA, the efficacy of chelated copper algicides in relation to water chemistry is poorly understood (Casitas Municipal Water District, 1987).

9.2.3 Use of oxidants

Potassium permanganate has been used as an algicide from as early as 1935 (Holden, 1970). A survey of North American utilities indicated that a small number use potassium permanganate relative to those who use copper sulphate (Casitas Municipal Water District, 1987). Commercial formulations of potassium permanganate marketed specifically as algicides are available in the USA (Casitas Municipal Water District, 1987). Fitzgerald (1966) investigated the relative toxicity of potassium permanganate to eight species of algae and cyanobacteria and found the algicidal dose was in the range 1-5 mg l^{-1}, except for one green algae where up to 8 mg l^{-1} was required.

Chlorine is used mainly for control of algae in water treatment works but is also known to have been employed in reservoir situations (Holden, 1970). The effective dose rates are dependent on the chlorine demand of the water, but most algae are reported to be controlled by residues of free chlorine between 0.25 and 2.0 mg 1^{-1} (Holden, 1970).

9.2.4 When to use algicides

Because cyanobacterial toxins are primarily intracellular, algicides must be used with particular caution to avoid release of intracellular toxins. Algaecides should be used when cell numbers are low to avoid excessive toxins or taints following rupture of the cells. This should be checked by post-dosing monitoring. Algaecides may be used at higher cell numbers only if the reservoir can be taken out of supply until the toxins and taints degrade, or if treatment for removal of the toxins and taints is available. In the latter cases the use of algicide should be assessed against the capability for whole cell removal offered by treatment processes, because cell removal may be safer. It is important to know how effective the chosen algicide is in the specific waters. For example, copper may be less effective in waters with high dissolved carbonate or at alkaline pH.

Table 9.2 Distribution of microcystins during laboratory culture of *Microcystis aeruginosa*

Age of culture	Distribution of toxins (%)	
	Cells	Water
Young		
Slowly-growing cells	100	0
Rapidly-growing cells	75-90	10-25
Old		
Slowly-growing intact cells	70-80	20-30
Decaying cells (leaking cell contents)	30-40	60-70

Source: National Rivers Authority, 1990

Algaecides should only be used in waters where the environmental impacts are acceptable and this should be checked with the local environmental agency.

9.3 Efficiency of drinking water treatment in cyanotoxin removal

Cyanobacterial toxins represent a challenge to drinking water treatment which involves removal of organic substances in both soluble and insoluble form. Water treatment processes may remove target substances by either separation or conversion. Separation processes are those which remove the target substance from the treated water, usually to a treatment residual which becomes a waste stream for disposal. Conversion processes involve transforming the target substance into a different chemical form, thereby reducing the water quality problem. Although conversion processes are sometime characterised as though they achieve destruction, there will always be reaction products and thus transformation is a more accurate description than destruction. Ideal conversion processes are those which yield innocuous reaction products.

A major factor in assessing water treatment for cyanobacterial toxin removal involves consideration of soluble and suspended substance removal. The primary toxins which have been studied, microcystins, nodularins and anatoxins, are all water soluble. However, laboratory observations for microcystins have shown that these toxins are produced within the cyanobacterial cells and are expected to be predominantly found within slow growing, healthy cells (Table 9.2).

Recent work (Mole *et al.,* 1997) has shown that microcystin release from cultured *Microcystis aeruginosa* began to occur late in the exponential growth phase and increased significantly during the stationary phase. This release was linked to a decrease in the integrity of the cells as determined by staining with fluorescein diacetate. The amount of toxin release was influenced by the culture medium and reached as much as 50 per cent in most commonly used media late in the stationary phase of population growth.

Until a bloom collapses or is otherwise affected by some treatment practice, the majority of toxins will be retained within the cells, making removal of intact cells a high treatment priority. However, under bloom conditions, a substantial proportion of toxin would also be expected to be released to the water column, making removal of soluble toxin an unavoidable concern.

Physicochemical treatment has been shown to cause cell lysis and toxin release (James and Fawell, 1991). Operational investigations in Africa demonstrated significant cell lysis during extended transport in pipelines (Dickens and Graham, 1995). However, other experiments conducted with cultured *Microcystis* showed that the flow and mixing conditions associated with water treatment did not cause cell lysis or toxin release. In addition, changes in pH from 5 to 9, which can occur in the treatment of some waters, did not cause any release of the intracellular toxins (WRc, 1996). Effects of physical and chemical stress on toxin release from cyanobacterial cells should therefore be assessed in treatment and conveyance systems.

The following sections review the capacity of established and novel treatment processes for the removal of cells and dissolved toxins.

9.3.1 Screening and prefiltration

Water treatment facilities usually employ coarse screens to remove debris from the water intake. These screens have no effect on the removal of either cyanobacterial cells or soluble toxins. However, microstrainers or fine screens may be used to remove larger algae, cyanobacterial cells and aggregated cells. Mouchet and Bonnélye (1998) reported removal rates of 40-70 per cent for two cyanobacterial species but pointed out that smaller species (e.g. single cells and small colonies of *Microcystis)* are poorly retained (to sometimes less than 10 per cent). Concerns regarding possible cell rupture, lysis and toxin release resulting from pressure on the filter screen have not been sufficiently addressed.

9.3.2 Aeration and air stripping

There are a number of methods for contacting air with water in drinking water treatment that may be required for various purposes, such as to oxidise iron and manganese from soluble to insoluble forms, to prevent reducing conditions which may yield odorous compounds, and to remove dissolved gases such as carbon dioxide, hydrogen sulphide, other reduced sulphur compounds and other volatile organic compounds (Hamann *et al.,* 1990).

Neither aeration nor air stripping will be effective for removing soluble toxins because they are non-volatile compounds. Nor would they be effective for removal of cyanobacterial cells (for aeration techniques applied in reservoirs to reduce growth of cyanobacteria see section 8.5.5).

9.3.3 Coagulation and clarification

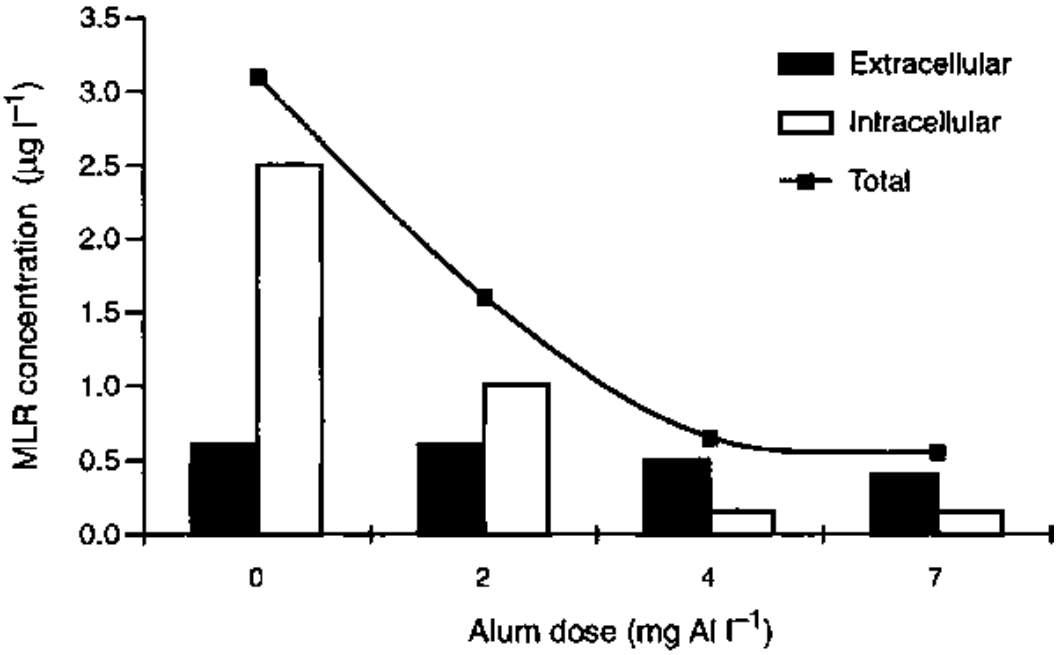
Coagulation promotes the aggregation of small, dispersed particles into larger particles which can be separated by sedimentation, filtration or flotation (Grohman *et al.,* 1985; Hamann *et al.,* 1990). Coagulation differs from precipitation because the latter involves converting soluble substances into insoluble particles, whereas coagulation deals with pre-existing dispersed particles such as mineral turbidity (clay, silt), larger molecular weight natural organic matter, micro-organisms including cyanobacteria, and oxidised, insoluble forms of iron and manganese.

Common chemicals used for drinking water coagulation include various aluminium and ferric iron salts. More recently synthetic organic polymers have gained some acceptance. Coagulation with multivalent metal salts can also be aided by adding various organic polymers to promote floe growth. Leuschner (1984) reported substantially improved flocculation of *Planktothrix agardhii* after addition of a cationic polymer. Efficient removal of algae is dependent on optimisation of chemical doses and coagulation pH. Mouchet and Bonnélye (1998) have shown that the coagulant dose necessary for algal removal is proportional to the sum of alkalinity and the logarithm of cell number. They emphasise that minimising turbidity in ajar test is not a sufficient criterion for adjusting treatment to remove algae and cyanobacteria, and recommend measuring the electrophoretic mobility of the cells (zeta potential) for optimising dosage (particularly because at insufficient coagulant dose, cyanobacteria will be the last phytoplankton cells to be removed). Bernhardt and Clasen (1991) have reported that coagulation of algal cells that are smooth and more or less spherical occurs largely by charge neutralisation. In

contrast, filamentous algae, large algae or species with bristles on their cell surface can be dealt with effectively only by sweep coagulation, by encountering the algae with large amounts of metal hydroxide floe.

Coagulation, by its nature, offers some promise for removal of intact cyanobacterial cells. For neurotoxins, Falconer (1989) reported that alum dosed at 120 mg l^{-1} alone and in combination with a number of polyelectrolytes removed about 20 per cent of the toxicity from a neurotoxic bloom of *Anabaena circinalis.* For microcystins, a number of published studies have shown that coagulation has a negligible capability for removal of any soluble toxins present in water. This has been demonstrated with aluminium sulphate coagulation jar tests in which total toxin concentration was reduced as a result of the removal of algal cells rather than the extracellular toxin (Figure 9.2) (WRc, 1996). Rositano and Nicholson (1994) also demonstrated this expectation by evaluating removal of purified, soluble microcystins by three coagulants: ferric sulphate, alum and polyaluminium chloride. In all cases they found essentially no toxin removal. Lambert *et al.* (1996) found inconsistent and low levels of microcystin removal (0-39 per cent) across the coagulation-sedimentation stage of a small, full-scale water treatment plant using an alum dose of over 60 mg l^{-1}.

Figure 9.2 The effect of coagulation with alum on the concentration of intra- and extracellular microcystin-LR (After Hart *et al.,* 1997. Reproduced courtesy of Blackwell Science)



By contrast, it must be emphasised that a study on raw water treatment with high doses of alum (200 mg l^{-1}) found over 23 per cent of the cell-bound microcystin-LR was released, mostly within two days of treatment (Lam *et al.,* 1995). However, at concentrations and conditions that would occur in water treatment plants, Velzeboer *et al.* (1995) found that aluminium sulphate did not appear to cause lysis of cells of cultured *Anabaena circinalis* or *Microcystis aeruginosa.* Flocculation under laboratory conditions, which simulated operating water treatment plants, resulted in removal of cells in a

healthy state, with no additional release of geosmin or microcystin-LR. Further work by Chow *et al.* (1997a) using ferric chloride as the coagulant showed similar results with some stimulation of growth of both algal species. There was no increase in concentration of microcystin in the water following treatment of *Microcystis aeruginosa,* although it appeared that *Anabaena circinalis* may be more susceptible to damage from chemicals. Later work using alum in a pilot plant with cultured *Microcystis aeruginosa* harvested at the late exponential phase of growth confirmed that the cells were not damaged through the treatment process and that no additional toxin was released during treatment (Drikas *et al.,* 1997). However, this study also confirmed that the low concentrations of extracellular microcystin present in the feed water (2-6 µg l^{-1}) are not removed during the treatment process. It was further found that the total cell number in sludge collected from the pilot plant decreased to half its initial value after two days, and that toxin release began virtually immediately, reaching almost 100 per cent after two days. After five days the toxin concentration began to decrease and was reduced by approximately 80 per cent after eight days and completely removed after 13 days. This corresponds to findings of Jones and Orr (1994) who observed that bacterial degradation of microcystin-LR occurred after nine days in a lake after chemical treatment of a *Microcystis aeruginosa* bloom. The importance of toxin release from sludge depends on the time that sludge is retained in sedimentation tanks and it could have implications for sludge management, particularly if supernatant is returned from sludge treatment processes to the head of the plant.

Selection of clarifier type will also affect cell removal rates. Mouchet and Bonnélye (1998) have summarised experience largely from warm climates and have shown that sludge blanket-type clarifiers are substantially more effective than static settlers (largely because of longer flocculation time), particularly if upflow pulsed systems are used. This achieved consistent reduction of total phytoplankton by 95-99 per cent at a plant treating Seine River water, 95-98 per cent elimination of cyanobacteria at a Philippine plant (as compared with 90-95 per cent removal by static settling), and 96.7-99.5 per cent removal of *Anabaena* and *Microcystis* at an industrial-scale plant in Harare (Zimbabwe). In Cairo and Alexandria, Egypt, older settling tanks were successfully upgraded to upflow pulsed sludge blanket clarifiers, thus not only improving performance for algal and cyanobacterial removal, but also efficiency per unit area and a reduction in coagulant consumption by 15-45 per cent and chlorine consumption by 15-35 per cent.

9.3.4 Dissolved air flotation

Although coagulation is normally followed by a sedimentation step, in some waters where the content of the suspended matter is low it is often easier to float the floe rather than attempting to settle a light floe. Recycled water saturated with air under pressure is introduced following the flocculation stage. Following the release of pressure the air comes out of solution and forms tiny bubbles which attach to the floe and cause it to float to the surface. The floated sludge is then collected and removed. This process is called dissolved air flotation (DAF) and is more effective than sedimentation, particularly for water with low turbidity and high colour, because the resultant floe is lighter and floats easily.

Dissolved air flotation is also generally more effective than sedimentation processes for treating algal-rich waters; for example floe blanket clarification has been shown to remove 76.5 per cent of *Microcystis* cells whilst DAF removed 98 per cent in the

presence of other algae (Gregory and Zabel, 1990). A Belgian DAF plant achieved 40-80 per cent removal *of Microcystis,* 90-100 per cent removal of Anabaena but only 30 per cent removal *of Planktothrix* (syn *Oscillatoria)* (Steffensen and Nicholson, 1994). Markham *et al.,* 1997) have reported on the efficiency of algae removal at eight DAF plants. Like Bernhardt and Clasen (1991), they observed that the characteristics of algae influence their removal by any clarification process. They found that most of the treatment plants produced more than 80 per cent removal and they expected this would be improved by optimisation. Vlaski *et al.* (1997) found that, in a pilot plant, DAF achieved high particle (algae) removal during a cyanobacteria bloom (mainly *Microcystis aeruginosa).*

Dissolved air flotation is unlikely to be more effective than conventional sedimentation processes for removing extracellular toxins. It may, however, remove more intact cells because the floating sludge tends to be removed more frequently than settled sludge in horizontal flow tanks, where the algae may die and then lyse. This assumption needs to be evaluated further.

Periods of high turbidity often cause problems for DAF, and any interruption in the process leads to an interruption in the treatment process. Thus a stock of spare parts and regular maintenance by qualified personnel are critical issues when using this approach (Mouchet and Bonnélye, 1998).

9.3.5 Precipitation for hardness reduction

Conversion of soluble compounds into insoluble particulates for separation by sedimentation or filtration is commonly used for water softening (calcium and magnesium removal) and for iron and manganese removal (Hamann *et al.,* 1990). Some concurrent removal of soluble metals and dissolved natural organic matter may also be achieved. Lime is commonly used for adjusting hardness or for precipitation of soluble metals. This process typically uses rapid mixing followed by flocculation and sedimentation.

No studies evaluating lime precipitation as a separate process in a water treatment plant sequence are available. However, some insight into the expected removal of intracellular toxins has been provided by two studies looking at treatment of raw water blooms with lime. Kenefick *et al.* (1993) found that lime doses from 100 mg l^{-1} as $Ca(OH)_2$ precipitated the cells in cyanobacterial bloom material containing microcystin-LR without releasing toxin compared with control batches over 14 days, while Lam *et al.* (1995) found only 4 per cent release of microcystin-LR for the same lime dosage. These studies suggest that lime softening would be effective at removing intracellular toxin by removing the cyanobacterial cells without causing cell lysis, but that there is no evidence to suggest that lime softening can reduce extracellular toxins.

9.3.6 Direct rapid filtration

Filtration is a process for the removal of suspended particulate matter, typically including clay, silt, natural organic matter, coagulated floes, lime softening precipitates, iron and manganese precipitates, and microorganisms (Hamann *et al.,* 1990). Filters most commonly use granular media such as coarse sand, crushed anthracite coal, garnet and granular activated carbon (GAC). Direct filtration is applied for low turbidity waters by

filtering directly after coagulation/destabilisation without an intervening clarification stage to remove the bulk of the floe. Conventional water treatment uses rapid filtration rates which require regular backwashing to maintain performance.

Mouchet and Bonnélye (1998) reported poor removal rates of 10-75 per cent, depending upon phytoplankton species, by direct rapid filtration without prior chemical treatment. Drikas *et al.* (1997) found that removal of *Microcystis aeruginosa* cells in the filtration stage of a pilot plant varied between 14 and 30 per cent following alum coagulation/sedimentation. Lepisto *et al.* (1996) evaluated full scale water treatment plants for their ability to remove cyanobacterial cells and found rapid sand filtration achieved only a 14 per cent reduction in cells. Rapid sand filtration, including GAC was somewhat better achieving 42 per cent reduction of cyanobacterial cells. These researchers expressed concern over the possible fate of intracellular toxins which may be released from degrading cells trapped in the filtration stage. Lambert *et al.* (1996) found inconsistent incremental removal of microcystins from 14-60 per cent across a dual media sand-anthracite filtration stage, following an alum coagulation-sedimentation stage, at a small, full-scale water treatment plant.

As an overall assessment of direct rapid filtration for elimination of algae and cyanobacteria, Mouchet and Bonnélye (1998) have indicated that direct filtration is generally not satisfactory, unless more sophisticated multimedia filters and adequate initial treatment are applied. They particularly emphasised the excellent results in algal removal after pre-ozonation (explicitly with the aim of enhancing cell removal through further steps, rather than for oxidation of cyanotoxins, see section 9.4.1).

A potential issue of concern, which currently has been inadequately investigated, is the effect of long filter runs between backwashing. Death and lysis of cyanobacteria retained on filters could lead to substantial toxin release.

9.3.7 Combined coagulation, sedimentation and rapid filtration

Conventional water treatment commonly involves the combination of coagulation, clarification (sedimentation or dissolved air flotation) and filtration. Consequently, much of the limited research that has been published on water treatment performance for the removal of cyanotoxins has looked at overall removal across the common combinations of coagulation-filtration and coagulation-clarification-filtration, rather than looking at each stage individually.

Himberg *et al.* (1989) evaluated hepatotoxic fractions from *Microcystis wesenbergii, M. viridis* and *Planktothrix agardhii* (syn. *Oscillatoria agardhii)* in bench-scale treatment processes consisting of alum or ferric chloride coagulation combined with sand filtration and chlorination. Alum coagulation, at doses from 36 to 71 mg l^{-1}, with filtration achieved toxin removals from 11 to 32 per cent, while ferric chloride at 55 mg l^{-1} achieved from 9 to 16 per cent. The removal contribution of the low chlorination dosage in this case was apparently negligible. They also studied a similar conventional process at pilot scale using freeze dried *Microcystis* bloom material and found negligible toxin removal (Keijola *et al.,* 1988). Nonetheless, Lambert *et al.* (1996) found combined microcystin removal was 50-60 per cent across coagulation, sedimentation and dual media filtration in a small full scale plant.

Similar studies at bench scale with anatoxin-a have indicated no removal for either alum or ferric chloride process combinations at a toxin concentration of 20 µg l^{-1}, but at 10 times higher toxin concentrations, the alum process achieved a 14 per cent anatoxin-a removal and the ferric chloride process achieved a 49 per cent anatoxin-a removal (Keijola *et al.,* 1988).

Leuschner (1984) studied phytoplankton retention by flocculation, sedimentation and rapid filtration in a plant treating highly eutrophic river water. Whereas *Microcystis* spp. (occurring as large colonies) were rarely observed in the finished water, *Planktothrix agardhii* was poorly retained, showing an average breakthrough of 27 per cent of the filaments. As also reported by Mouchet and Bonnélye (1998), addition of a cationic polymer during flocculation substantially improved retention.

The removal of whole, intact cells presents the best opportunity to remove toxins in separation processes, whereas the literature indicates removal efficiencies are low with extracellular toxins. Some unsatisfactory results reported with lysis of entire cells may have been due to an excessive time delay between flocculation and analysis. In summary, currently available results indicate that conventional coagulation and rapid filtration processes assist in toxin removal, particularly if cyanobacterial cells are kept intact, but cannot be generally relied upon as the main removal process. Mouchet and Bonnélye (1998) have emphasised the need for:

"... *pilot scale investigation in order to estimate the technical and economical advantages of this choice in each case. Generally, a conventional treatment line, including coagulation, flocculation, settling or flotation, and filtration, is preferred to treat algae-rich waters. However, algae removal is somewhat more delicate than turbidity removal and, consequently, greater attention is required when selecting technology and adjusting the chemical treatment.*" (Mouchet and Bonnélye, 1998)

9.3.8 Slow sand filtration

In contrast to rapid filtration, slow sand filters operate at lower rates and develop a surface filter cake which performs most of the filtration together with (often high) biological treatment activity. These biofilms establish after some time of operation and contribute significantly to degradation of dissolved substances. Mouchet and Bonnélye (1998) reported a likely removal of 99 per cent of algal cells by slow sand filtration. Operation of these filters in the dark can prevent intensive algal growth on the filter. However, overloading of filters with algae or cyanobacteria from the raw water may lead to rapid blocking, requiring removal of the bioactive surface layer, thus temporarily reducing the efficiency for retention of dissolved substances. For removal of toxic cyanobacteria, this constitutes a dilemma because bloom-containing waters are likely to lead to rapid blocking and thus undermine the practicability of slow sand filtration. However, experiments have shown that before blocking, slow sand filters may be quite effective in the removal of toxic cyanobacteria and dissolved toxins.

Keijola *et al.* (1988) evaluated laboratory-scale slow sand filters and reported over 80 per cent removal of toxins from *Microcystis,* 30-65 per cent removal of toxins from *Planktothrix* (syn. *Oscillatoria)* and about 70 per cent removal of anatoxin-a. Because filtration itself would not be expected to achieve any removal of extracellular toxin, these results suggest that the mechanisms were at least biosorption, and perhaps some

biotransformation. Australian studies (Sherman *et al.,* 1995) with roughing filters followed by slow sand filters showed that *M. aeruginosa* and some *Planktothrix* (syn. *Oscillatoria)* cells from toxic bloom material could be removed by physical means and biological processes. Superior microcystin removal, in one of two river water sources being treated with GAC filters, was attributed to biological activity (Drikas, 1994). Freeze dried bloom material was used in this study.

Work on microcystin-LR degradation using an isolated bacterium for use in water treatment has been undertaken by Bourne *et al.* (1996). A pseudo-monad has been isolated which possesses an enzyme system capable of degrading microcystin, but the work is currently only at the laboratory scale. Pilot plant studies using a solid phase support for this bacterium to investigate this process are to be undertaken.

Developments have occurred in the exploitation of slow sand filters at large treatment works, notably in the UK and Netherlands. These have included use of various pretreatments, such as conventional treatment by coagulation and filtration and pre-ozonation to control the rate of blocking by algae and cyanobacteria. Whilst these processes will assist with removal of cells containing toxins, they have not been adequately assessed for their reliability in degradation of extracellular toxins. A notable development has been the sandwiching of a layer of GAC within the bed of sand in slow sand filters in order to assist in removal of dissolved toxins.

General experience with slow sand filters suggests that they are potentially very useful for removal of particles and dissolved substances, particularly if further developed or combined with other treatment steps to avoid blocking when loaded with waters rich in algae and cyanobacteria (or other particles). New approaches to slow sand filtration are experimenting with horizontal rather than vertical water flow (as used in cross-flow membrane techniques). This requires larger amounts of water but will remove most of the potentially filter-blocking particles and, in particular, would keep cyanobacteria suspended. Such systems may be developed locally, particularly to serve small communities. For large treatment facilities, bulk cell removal by coagulation and clarification before slow sand filtration may be an effective approach for obtaining the benefits while avoiding rapid blocking.

9.3.9 Activated carbon adsorption

The use of activated carbon adsorption has expanded greatly in Europe and North America during the past two to three decades because most other water treatment processes are ineffective in removing soluble organic matter. This approach uses either powdered activated carbon (PAC) which can be added intermittently whenever the need arises or GAC adsorbers which are used continuously. Accordingly, GAC may be more expensive than PAC when used only intermittently, but it is also generally more effective and more reliable for consistent removal of soluble organic compounds (Hamann *et al.,* 1990). Given the nature of cyanobacterial toxins, activated carbon adsorption would be expected to offer some promise for toxin removal.

Powdered activated carbon

Keijola *et al.* (1988) found that 20 mg l^{-1} of PAC was able to achieve a 90 per cent removal of hepatotoxins following conventional treatment combined with pre-ozonation.

Hart and Stott (1993) and Croll and Hart (1996) have reported the evaluation of several PACs for the removal of microcystin-LR at an initial concentration of 40 µg l^{-1}. With the most effective PAC tested (wood based), doses greater than 20 mg l^{-1} were required to achieve toxin removal of greater than 85 per cent.

Donati *et al.* (1993) also evaluated several different PACs for the removal of dissolved microcystin-LR at an initial concentration of 50 µg l^{-1}. For the best PAC they studied, a dose of 25 mg l^{-1} with 30 minutes contact time was able to achieve 98 per cent removal, while for the poorest a dose of 50 mg l^{-1} only achieved a 60 per cent removal. They suggested that the mesopore volume of the various carbons was the best predictor of carbon performance (Donati *et al.,* 1994a). Nodularin was also removed with PAC (Donati *et al.,* 1994b). Likewise, Bernazeau (1994) found that 12 mg l^{-1} of PAC could achieve a 95 per cent reduction of dissolved microcystin-LR from an initial concentration of 50 µg l^{-1}. Monitoring of a full scale conventional water treatment plant which was using a PAC dose of 30 mg l^{-1} showed the combined treatment processes removed an average of 82 per cent when microcystin levels in raw water were above 0.5 µg l^{-1} (Lambert *et al.,* 1996).

There is general agreement that to achieve high removal efficiencies, very high doses of PAC are required for toxin removal and that contact time is very important. Lower doses of PAC are required with pure water compared with natural water containing organic matter and when using actual plant mixing conditions and contact times. Alum coagulation in conjunction with PAC was also found to affect adversely toxin removal (Jones *et al.,* 1993).

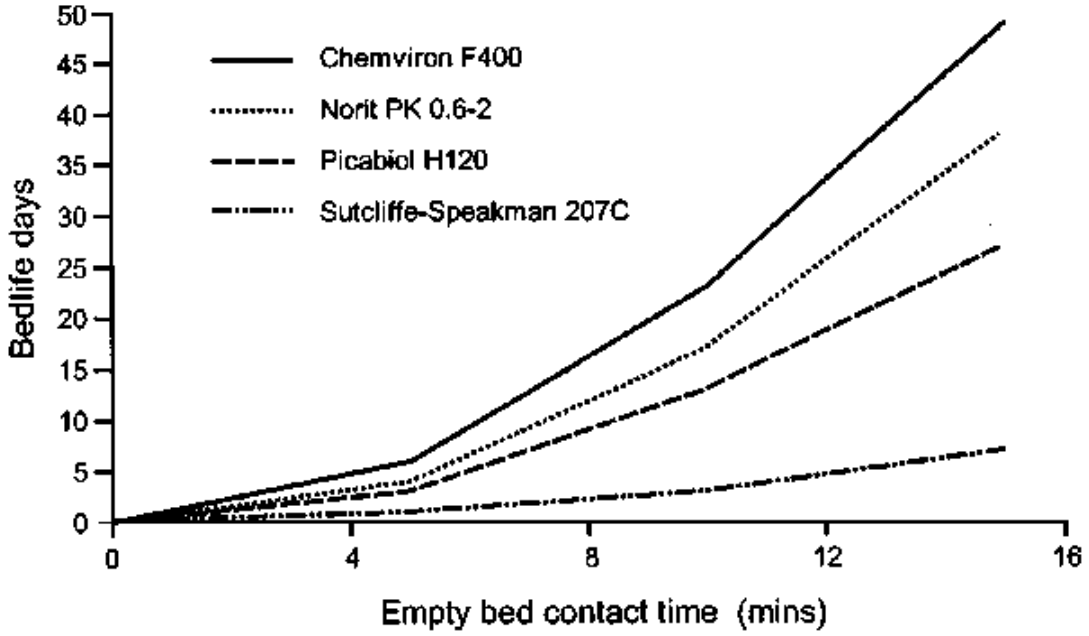
Granular activated carbon

As might be expected, research into the performance of GAC has shown effective removal of toxins, provided the adsorption capacity of the GAC has not been compromised. Pilot scale tests treating microcystins at 30-50 µg l^{-1} showed greater than 90 per cent toxin removal for water treatment volumes up to 7,000-10,000 activated carbon bed volumes before efficiency dropped to less than 63 per cent (probably because of saturation of the GAC with dissolved organic carbon (DOC)) (Bernezeau, 1994). In these trials, the raw water had DOC levels at 5-6.5 mg l^{-1}, more than 100-fold greater concentration than the microcystins. The DOC: toxin ratio would be at least this high under any realistic bloom conditions.

Studies by Hart and Stott (1993), using rapid column tests to simulate the performance of GAC under dynamic conditions predicted bedlives to be fairly short for continuous exposure to microcystin concentrations of 5-20 µg l^{-1}. For example, Figure 9.3 shows predicted bedlife for four different carbons, based on rapid column tests. The bedlife is the time taken to reach 1 µg l^{-1} in the treated water with a constant concentration of 10 µg l^{-1} in the feed water, for a range of empty bed contact times (EBCTs). For EBCTs typically used in water treatment of 10-15 minutes, the best performing carbon for this water gave a bedlife of only 30-45 days. These results were confirmed in Australian studies by Jones *et al.* (1993) and Craig and Bailey (1995) in both laboratory and pilot plant studies, using air dried bloom material. The results showed that while various GACs were effective for microcystin-LR removal, the life of the GAC was limited. Saturation conditions probably explain the observations that a full-scale GAC adsorber was achieving only between 40 and 60 per cent microcystin removal down to 0.6-1.2 µg

l^{-1} for raw water which typically had DOC levels of 20 mg l^{-1}, 2,000 fold greater than the toxin levels (Lambert *et al.,* 1996).

Figure 9.3 Predicted GAC bedlives for 10 µg l^{-1} microcystin-LR input and 1 µg l^{-1} limit in filtrate from rapid column test results for four different carbons (After Carlisle, 1994. Reproduced courtesy of the Foundation for Water Research, UK)

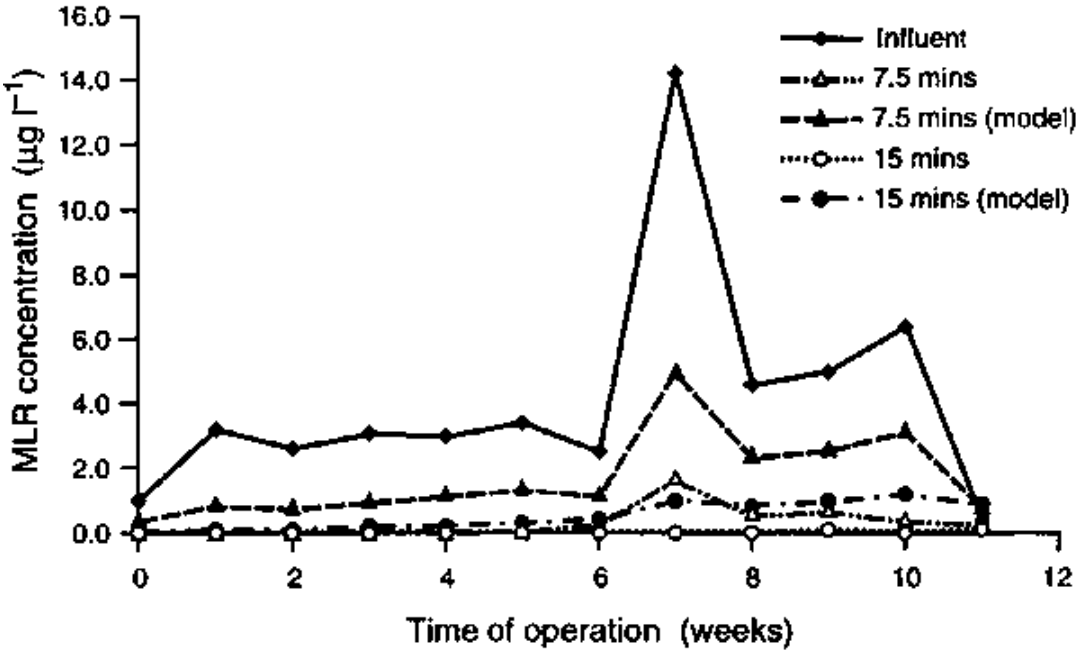


No published studies have been found using GAC specifically for removal of nodularin, cylindrospermopsin or PSP toxins. However, a report by Falconer *et al.* (1989) showed removal of *Anabaena* neurotoxicity on GAC. Given the later identification of the toxin of the population studied, their study almost certainly assessed PSP toxin removal. Carlile (1994) repeated the tests by Hart and Stott (1993), using the GAC they found to be most effective, and found anatoxin-a to be adsorbed better than microcystin-LR.

Biologically active carbon

Granular activated carbon is not only an effective adsorption process but it is also an effective medium for biological treatment. Because microcystin-LR has been shown to be biodegradable (Fawell *et al.,* 1993), it is therefore possible that the toxin could be degraded on a biologically active GAC. Carlile (1994) undertook pilot scale tests using two GACs, one that had been previously used on a pilot plant for total organic carbon (TOC) removal and an unused GAC. For the tests, for each GAC, two different contact times of 7.5 and 15 minutes were used. The pilot plant results showed that there was no significant difference between the performance of the unused GAC and the used GAC at both contact times. However, the comparison of pilot plant results with results of modelling assuming removal only by adsorption, shows poorer removal by adsorption only (without any biological activity) at both contact times (Figure 9.4). The implications from this are that the better removal on the pilot plant resulted from biological activity on the GAC, and that this biological activity developed very quickly also on the unused GAC.

Figure 9.4 Comparison of pilot scale test results for microcystin-LR removal by used GAC (probably biologically active) with performance predicted from models for adsorption only (After Hart *et al.,* 1997. Reproduced courtesy of Blackwell Science)



Pilot plant trials investigating anatoxin-a removal by GAC showed no breakthrough, whereas modelled results for the same operating conditions predicted breakthrough (UK WIR, 1995). This suggested that biological activity was also important for anatoxin-a removal by GAC.

In practice, it is difficult to exclude biological activity from GAC adsorbers and therefore better removal of both toxins than indicated by rapid column tests would be expected. The pilot-scale experiments discussed above suggest that when biological activity is established, GAC at 15 minutes effective bed contact time provides a high degree of security for both microcystin-LR and anatoxin-a removal. However, as these results currently are poorly confirmed in full scale application, careful surveillance of treatment performance is essential for treatment plants removing cyanotoxins in the raw water with GAC. This particularly pertains to monitoring of breakthrough when saturation with DOC is approached.

9.4 Chemical oxidation and disinfection

Drinking water is treated with chemical oxidants to fulfil a wide variety of objectives including: control of biofilm growth, colour removal, odour control, enhancement of coagulation and flocculation, and iron or manganese oxidation. The most critical application of chemical oxidants is for disinfection. The chemicals used most commonly in municipal water treatment are chlorine, chloramines, ozone, chlorine dioxide and potassium permanganate.

9.4.1 Oxidation combined with disinfection

Once cyanobacterial cells have been removed from water, dissolved cyanotoxins are potentially susceptible to oxidation by disinfectants. Several substances have been tested for this purpose in drinking water treatment.

Chlorine

Early work reported that substantial doses (5 mg l^{-1}) of chlorine were ineffective in destroying toxicity from algal extracts, as measured in mouse bioassays (Hoffman, 1976). Likewise, combined treatment processes which included chlorination at 0.5 mg l^{-1} were also found ineffective, suggesting little contribution from the chlorination stage (Keijola *et al.,* 1988; Himberg *et al.,* 1989). Similarly, Lambert *et al.* (1996) found that chlorination achieved negligible reduction in microcystin levels of 0.3-0.5 µg l^{-1} in treated water. In these studies, chlorine may have been consumed rapidly by the high concentrations of organic matter reported to be present, leaving insufficient available for removal of microcystins. However, Nicholson *et al.* (1994) showed that chlorination could be very effective at destroying microcystin-LR and nodularin under the correct treatment conditions, i.e. free chlorine residual of 0.5 mg l^{-1} after 30 minutes contact time with pH < 8. In contrast, they found that chloramination was completely ineffective at destroying microcystin-LR and nodularin, and this creates a problem for treating natural waters with any substantial nitrogenous chlorine demand.

Carlile (1994), Croll and Hart (1996) and Hart *et al.* (1997) have reported tests with a variety of oxidants using water spiked with dissolved microcystin-LR or anatoxin-a in the range 5-10 µg l^{-1}. The tests with chlorine used an applied dose of 1.7 mg l^{-1}, which was found to give a free residual of approximately 0.7 mg l^{-1} after 30 minutes. The effectiveness of the chlorine in reducing microcystin-LR concentration was very dependent on pH and time. At pH 5, removal was more than 93 per cent within 30 minutes whilst at pH 7 removal reached only 88 per cent after 22 hours. Tests with a water containing Microcystis cells indicated that chlorination could be similarly effective. Chlorination during treatment at a pH sufficiently low to show maximum effect might not be feasible in practice. However, in conjunction with extended contact times with a residual free chlorine concentration, microcystin is likely to be degraded. Monitoring of this effect is important.

Chlorination tests have also been undertaken with water containing dissolved anatoxin-a. Nicholson *et al.* (1994), as well as Carlile (1994), reported no discernible removal of anatoxin-a by chlorination. Rositano and Nicholson (1994) also showed that chlorination of anatoxin-a was ineffective with a dose of 15 mg l^{-1} at pH 7 for 30 minutes contact time, providing only a 16 per cent removal. Recent Australian studies (unpublished results) have shown that removal of cylindrospermopsin can be achieved with chlorine doses of 1-2 mg l^{-1} at pH levels between 6 and 7.5 and a chlorine residual of 0.5 mg l^{-1}.

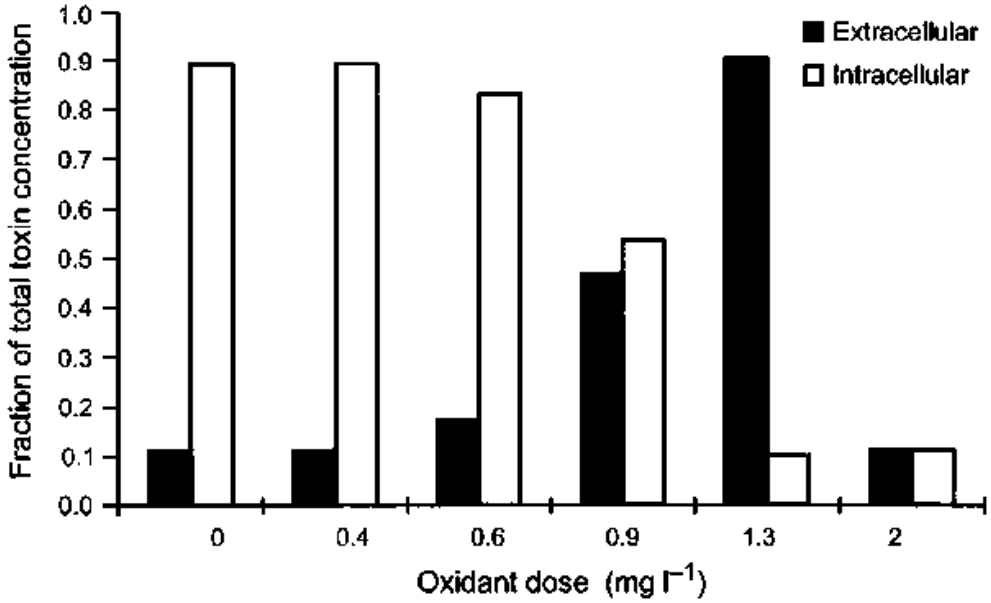
Care must be taken with chlorination procedures to avoid occupational exposure to toxic levels of chlorine in the air, or the formation of excess levels of trihalomethanes.

Ozone

The most consistently efficient process for destruction of both ultra- and extracellular microcystins appears to be ozonation, which can rapidly achieve essentially complete destruction of microcystins, nodularin and anatoxin-a (Keijola *et al.,* 1988; Himberg *et al.,* 1989; Rositano and Nicholson, 1994; Croll and Hart, 1996; Rositano *et al.,* 1996; Hart *et al.,* 1997). The major consideration in the application of ozonation is the ozone demanded by background DOC concentrations because, at a DOC level of 8.5 mg l^{-1}, ozone doses above 1 mg l^{-1} were necessary to achieve complete microcystin-LR destruction (Rositano and Nicholson, 1994). The results of Hart *et al.* (1997) demonstrate the importance of sufficiently high ozone doses (Figure 9.5). At low doses up to 0.6 mg l^{-1}, ozone degraded DOC and had little effect on microcystin-LR. Only after the DOC demand was satisfied, did the ozone show an effect on microcystin-LR. However, between 0.6 and 1.3 mg l^{-1}, this effect consisted almost entirely of cellular lysis, and only at 2 mg l^{-1} was extracellular toxin subsequently converted. These results highlight the crucial importance of sufficiently high ozone doses as well as of careful monitoring of performance, particularly with variable DOC concentrations in the water source as occur during cyanobacterial blooms. As discussed in section 9.4.2, the performance of ozone may be improved substantially if it is applied in several steps, e.g. before destabilisation/flocculation as well as after filtration.

Recent work in Australia (unpublished results) has shown that the ozone dose necessary to achieve removal of a range of PSP toxins in the concentration range 10-100 µg l^{-1} was less than the ozone demand of the water. Other recent studies in Australia (unpublished results) have shown that ozone is also effective for the removal of cylindrospermopsin.

Figure 9.5 Effect of ozonation on the distribution of both intra- and extracellular microcystin-LR from *Microcystis* dosed into a raw lowland water (After Hart *et al.,* 1997. Reproduced courtesy of Blackwell Science)



Care must be taken with ozone procedures to avoid occupational exposure to toxic levels in the air.

Potassium permanganate

Potassium permanganate at 1 mg l^{-1} was found to achieve 95 per cent removal of microcystin-LR in 30 minutes. However, in the presence of live intact cells removal was much poorer, suggesting that permanganate was unable to penetrate or lyse the cells effectively and was therefore unable to come into contact with the toxin (Rositano, 1996). Hart and Stott (1993), Carlile (1994), Croll and Hart (1996) and WRc (1996) have all reported similar observations for the removal of dissolved microcystin-LR and anatoxin-a and the same limitation in treating *Microcystis* cells. Lam *et al.* (1995) reported that potassium permanganate caused some cell lysis and liberation of microcystin-LR. This finding may be influenced by longer contact times than those used by Rositano (1996).

Hydrogen peroxide and UV radiation

Hydrogen peroxide was found ineffective in toxin removal, whereas either UV alone or UV with hydrogen peroxide achieved about a 50 per cent removal of microcystin-LR after 30 minutes (Rositano and Nicholson, 1994).

In contrast, Croll and Hart (1996) and WRc (1996) found UV radiation was capable of efficiently degrading both microcystin-LR and anatoxin-a, but only at very high doses of about 20,000 mWs/cm^2. A typical water disinfection dose is about 30 mWs/cm^2, and therefore UV on its own cannot be regarded as a practical method of toxin reduction. A recent finding has shown that very high concentrations of microcystin-LR (50-200 mg l^{-1}) were rapidly (10-40 minutes) destroyed using UV light in the presence of a titanium dioxide catalyst (Robertson *et al.,* 1997). The potential applications of this finding in water treatment remain to be explored.

Chlorine dioxide

Chlorine dioxide has strong oxidising ability, although only limited studies have been conducted with this oxidant. Hart and Stott (1993) found that whilst a dose of 6 mg l^{-1} was required to reduce 4.6 µg l^{-1} of dissolved microcystin-LR to less than 1 µg l^{-1}, a dose as great as 10 mg l^{-1} had no effect on about 4 µg l^{-1} of intracellular microcystin.

9.4.2 Pre-oxidation (before cell removal)

Pre-oxidation has been widely reported to assist coagulation, especially in the removal of some algae and cyanobacteria. Oxidants have been shown to breakdown some cyanotoxins effectively under certain conditions (see section 9.4.1) but may also lead to cell lysis and toxin release. Thus pre-oxidation of toxic cyanobacteria is a highly critical issue in treatment design.

Ozone has been most effective in oxidation of cell-bound microcystin, if applied at a sufficiently high dose and contact time (see section 9.4.1). Dissolved air flotation has been proposed in which the recycled water is saturated with ozone-rich air (Baron *et al.,* 1997). Ozone-rich air has also been proposed to be used in dispersed air flotation.

These approaches might result in reduction of extracellular toxin as well as enhanced removal of cells.

Chlorine has been applied to destroy cell-bound microcystins before further treatment. However, Lam *et al.* (1995) showed that chlorination of bloom material using a high dose of 44 mg l^{-1}, resulted in release of 64 per cent of the intracellular microcystin. Thus, pre-chlorination of raw waters containing cyanobacterial cells risks the release of toxin from otherwise intact cells.

Mouchet and Bonnélye (1998) have compared pre-ozonation and pre-chlorination with respect to their effect in elimination of algae and cyanobacteria, as well as toxin release and formation of by-products. They concluded that pre-chlorination is slightly more effective than pre-ozonation in enhancing coagulation (96.9 per cent removal as compared with 94.1 per cent in one treatment plant in France). However, this advantage is offset by the problems of cell damage resulting in release of DOC and metabolites which either may be toxic or may impart offensive taste and odour, as well as leading to formation of by-products (particularly highly unpleasant chlorophenols). In contrast, for pre-ozonation (usually dosed at 1 mg l^{-1}) these authors found little, if any, cell lysis at doses up to 3 mg l^{-1}. They recommend pre-ozonation as the better choice, especially in conjunction with a main ozonation step further in the treatment line, e.g. between clarification and filtration. It is however acknowledged that pre-chlorination is still very common, particularly in developing countries. While the advantages for improving clarification, keeping filters clean, eliminating ammonia and enhancing post-chlorination are well established, pre-chlorination in plants without subsequent adsorption onto activated carbon is not recommended.

Prior to cell removal, the total and dissolved organic carbon load of water with cyanobacterial blooms will vary by orders of magnitude, and consumption of the oxidant will therefore also vary widely. Continuous control of the oxidising step and very high doses may be necessary to ensure complete oxidation of cyanotoxins in one pre-treatment step. This is likely to be difficult in practice, and is associated with a risk of toxin liberation. Removing cyanobacterial cells before application of oxidant is safer. In contrast, pre-oxidation with a low ozone dose may be useful because it substantially enhances cell removal by subsequent steps. Safe and effective operation is possible if further cyanotoxin barriers (such as a further ozone step or GAC) are available. Consequently, pre-oxidation may be regarded as a step for enhancement of cell removal rather than cyanotoxin degradation, and requires either monitoring for breakthrough of dissolved toxins during cyanobacterial blooms or for the use of further multiple barriers in the treatment system.

9.5 Membrane processes and reverse osmosis

Membrane processes, particularly microfiltration (MF) and ultrafiltration (UF) are increasingly seen, under some circumstances, as economically viable treatment alternatives to conventional treatment for small and large communities. They should be effective in the removal of cyanobacteria and intracellular toxins.

Experimental studies at laboratory scale with flat-sheet UF and MF membranes, in both dead-end and crossflow modes, have shown high efficiency of removal (> 98 per cent) of whole cells of toxic *M. aeruginosa* (Chow *et al.,* 1997b). This study also examined the

effect of the filtration process on cell integrity by fluorescence microscopy and assessed cell damage by measuring the leakage of cell chlorophyll and toxin (microcystin-LR) into the permeate. There was evidence of damage to a small proportion of cells following filtration, but no significant increase in toxin in the permeate with all modes of filtration. In experiments with the ultrafiltration membrane, the amount of microcystin was significantly lower in the permeate than in the feed, which suggested that the particular UF membrane employed may have rejection properties or adsorption ability for microcystin. This would not be expected for UF membranes although removal of soluble toxin may be achieved with a very low molecular weight cut-off pore size, such as those offered by nanofiltration membranes. Hart and Stott (1993) evaluated the effect of nanofiltration for the removal of microcystin spiked into natural water at concentrations between 5 µg l^{-1} and 30 µg l^{-1} and found removal to below 1 µg l^{-1}. Australian studies with membranes (Muntisov and Trimboli, 1996) also showed that using nanofiltration microcystin-LR and nodularin at 8 µg l^{-1} were removed from water from the River Murray that had been spiked with toxin.

Neumann and Weckesser (1998) have tested three reverse osmosis membranes at 25-35 bar for elimination of microcystin-LR and microcystin-RR from tap and salt (3,000 mg l^{-1} NaCl) water. Initial toxin concentrations in the retentate were in the range 70-130 µg l^{-1}. With a detection limit of 0.2 µg l^{-1}, average retention levels were 96.7-99.6 per cent. There was no statistical difference in retention of the microcystins between the two waters.

9.6 Microcystins other than microcystin-LR

Most of the published research relates to microcystin-LR, even though its concentration can be exceeded by those of other variants, or by the sum of the concentrations of other variants (Codd and Bell, 1996).

Computer models are available which can be used to predict the properties of chemical compounds, based on their chemical structure, in order to provide information in relation to toxicology and environmental impact. Such models have been used to predict the properties of the microcystin variants which would be important in relation to removal by water treatment processes (WRc, 1997).

A physical measure of solubility and interaction with water molecules that gives an indication of the potential adsorption by activated carbon is the octanol-water partition coefficient, K_{ow}. This is defined as the ratio of the concentration in the octanol phase to the concentration in the water phase in a two-phase octanol-water system at equilibrium, and is usually expressed as a logarithm. Readily adsorbed, hydrophobic compounds have high values and poorly adsorbed hydrophilic compound have low values (often negative, indicating a higher concentration of the compound in the water phase). K_{ow} values have been estimated from molecular structure to provide an indication of the relative hydrophobicity compared with microcystin-LR (for which some information on activated carbon adsorption is available). The calculated K_{ow} values suggest that the majority of variants would be adsorbed by activated carbon similarly to, or better than, microcystin-LR. Hence any strategy for using activated carbon, based on the data available for microcystin-LR, would probably be suitable for the majority of the other microcystins.

Attempts to model the reactivity of microcystin variants with oxidants have been unsuccessful because of the complexity of the molecular structure. A principal mechanism of action of oxidants, particularly ozone and chlorine, on organic compounds is by the breakdown of double bonds. Any modifications to the basic microcystin structure which increases the degree of double bonding in the molecule would therefore be expected to enhance its reaction with ozone or chlorine. It has been concluded, from consideration of the amino acid functional groups in the variants, that some variants would be expected to be more reactive with oxidants than microcystin-LR, although the effect may not be important in practical terms because the basic molecular structure is not changed radically. For the same reason, the other variants would not be expected to be much less reactive with oxidants than microcystin-LR. Hence, any strategy for oxidant application based on microcystin-LR data would probably be just as effective for the other microcystins.

The modelling approach available for biodegradability can only class compounds as biodegradable or non-biodegradable, and cannot provide any further quantification to the degree of biodegradability. Modelling has classed microcystin-LR as biodegradable, and changes to the amino acids have not changed this classification. Hence all the variants would be expected to show similar biodegradability to microcystin-LR. This would be of significance in relation to the performance of biological GAC and slow sand filtration processes.

The lack of experimental data on the elimination of microcystins other than microcystin-LR emphasises the need to monitor performance of any treatment system that is applied for cyanotoxin removal.

9.7 Effective drinking water treatment at treatment works

There are a number of messages that arise from the published work with respect to good practice as well as effective design and operation of water treatment works. These include:

- Resources and abstraction should be managed to minimise the presence of algal concentrations in the raw water delivered for treatment.

- Chemical preparation and dosing facilities must be of adequate size, process control should ensure rapid dispersion and appropriate retention times, and chemical doses should be optimised at the appropriate pH.

- Some oxidants, e.g. ozone, can be dosed before coagulation and clarification but require particular care, not only to avoid lysis of cells but also to limit problems with disinfection by-product formation. Separation of steps into a low pre-oxidation dose to enhance flocculation and a higher dose after cell removal to oxidise dissolved toxins is a safer approach.

- Granular activated carbon plants with a high EBCT and ozone-GAC facilities may remove toxins effectively, especially if the GAC supports substantial biological activity.

- The effectiveness of treatment plants without ozone but with GAC will depend on the GAC EBCT value, on the degree of biological activity on the GAC, on the extent of exhaustion of the GAC and of the magnitude and duration of toxin occurrence.

- Conventional treatment plants without ozone and GAC might remove cyanobacterial cells and dissolved toxins satisfactorily if coagulation, clarification, filtration and superchlorination-dechlorination (with a contact time of>15 mg min l^{-1}) or ozonation are carried out effectively.

- Slow sand filter plants remove algal cells effectively, although pre-treatment steps are generally applied to maximise filter runs and efficiency. Because of the biological activity in slow sand filters and long contact times, some removal of dissolved toxin should be expected but this capability is unclear. Slow sand filter plants with pre-ozonation and/or sand-GAC sandwiching would be expected to be effective for dissolved toxins (although confirmation of this expectation is needed).

- Frequent monitoring of treatment performance is crucial to ensure safety, particularly with respect to cyanotoxin removal, because available information on the performance of different treatment steps is specific to the conditions of the experiments reported, and performance under other conditions is unclear. Variable and often high loads of DOC during cyanobacterial blooms may rapidly compromise treatment procedures that were initially successful.

- Most procedures have been studied for cyanotoxin removal as isolated treatment steps, rather than as a combination following the multi-barrier principle. Planning of treatment will lead to best results if combinations are considered, and if cell and dissolved toxin removal are separately evaluated (e.g. combinations of pre-oxidation to enhance cell removal with effective post-oxidation to ensure destruction of liberated toxin, or combinations of cell removal and slow sand filtration).

Perhaps because of the intermittent nature of cyanobacterial blooms, very little information has been reported from full-scale treatment plants treating water at naturally occurring toxin levels. Laboratory and pilot-scale investigations have shown that dissolved toxins can be removed effectively to less than 1 µg l^{-1} under conditions normally used in water treatment by biologically active GAC, ozone, potassium permanganate and chlorine (microcystin only). The information which has been reported to date is summarised in Table 9.3.

Table 9.3 Summary of water treatment performance on microcystins

Treatment technique	Expected removal[1]		Comments
	Cell bound	Extracellular	
Coagulation/sedimentation/dissolved air flotation	> 80%	<10%	Removal only achievable for toxins in cells, provided cells are not damaged
Precipitation/sedimentation	> 90%	<10%	Removal only achievable for toxins in cells, provided cells are not damaged
Rapid filtration	> 60%	<10%	Removal only achievable for toxins in cells, provided cells are not damaged
Slow sand filtration	~ 99%	Probably significant	Removal effective for toxins in cells; efficiency for dissolved microcystin is likely to depend on biofilm formation and thus on filter run length
Combined coagulation/sedimentation/filtration	> 90%	< 10%	Removal only achievable for toxins in cells, provided cells are not damaged
Dissolved air flotation	> 90%	Not assessed, probably low	Removal only achievable for toxins in cells, provided cells are not damaged
Adsorption - Powdered activated carbon (PAC)	Negligible	> 85%	For adequate PAC doses (> 20 mg l^{-1}) with a PAC shown to be effective, DOC competition will reduce capacity
Adsorption - Granular activated carbon (GAC)	See rapid filtration	> 80%	For practical EBCTs, DOC competition will reduce capacity and hasten breakthrough, filtration also removes algal cells
Biological granular activated carbon	See rapid filtration	> 90%	See GAC, biological activity enhances removal efficiency and bed life
Pre-ozonation	Very effective in enhancing coagulation	Potential increase	Useful in low doses to assist coagulation of cells; risk of toxin release requires careful monitoring and possibly subsequent treatment

			steps
Pre-chlorination	Very effective in enhancing coagulation	Causes lysis and release of dissolved metabolites	Useful to assist coagulation of cells but applicable for toxic cyanobacteria only if subsequent treatment steps will remove dissolved toxins and other released metabolites
Ozonation (post clarification)	-	> 98%	Rapid and efficient on soluble toxin provided that DOC demand is satisfied
Free chlorine (postfiltration)	-	> 80%	Effective when free chlorine is > 0.5 mg l^{-1} after > 30 minutes at pH < 8 and low DOC; effect negligible when dose low or pH > 8
Chloramine	-	Negligible	Ineffective. Free chlorine application will yield ineffective chloramines in waters enriched with nitrogenous organic matter
Chlorine dioxide	-	Negligible	Not effective with doses used in drinking water treatment
Potassium permanganate	-	95%	Effective on soluble toxin but only in absence of whole cells
Hydrogen peroxide	-	Negligible	Not effective on its own
UV radiation	-	Negligible	Capable of degrading microcystin-LR and anatoxin-a, but only at impractically high doses
Membrane processes	Likely to be very high (> 99%)	Uncertain	Depends on membrane type, further research required to characterise performance

DOC Dissolved organic carbon

Source: Adapted from Yoo *et al*., 1995

[1] Likely efficiency of removal when continuously applied at optimal doses and pH and under proper operating conditions

9.8 Drinking water treatment for households and small community supplies

Domestic upgrading of piped drinking water supplies has been a recent issue of concern in some countries. Many central supplies provide excellent quality drinking water and additional household treatment may actually cause deterioration rather than improvement. However, domestic treatment may have a role in regions supplied with poor quality drinking water, or for especially sensitive sub-populations. Furthermore, in many parts of the world, simple and easily maintained treatment for households and small communities may improve the quality of water otherwise used for drinking without any treatment. Boiling water will not remove or degrade cyanotoxins (Chen *et al.,* 1998).

Lawton *et al.* (1998) tested three different domestic jug filtration units for their capacity to remove extracellular microcystins (LR, LY, LW and LF) and one unit for removal of intact cells *(Microcystis aeruginosa* as single cells, spiral filaments of *Anabaena flos-aquae* and straight filaments of *Planktothrix* (syn. *Oscillatoria) agardhii).* Treatment in the jug units is based on activated carbon and ion exchange resins. Whereas approximately 60 per cent of the filamentous cyanobacteria were removed, 90 per cent of the single cells of *Microcystis* passed through the filter (removal of large *Microcystis* colonies was not tested but may be more effective). Cell morphology was thus considered crucial for elimination performance. Removal of microcystin variants ranged from 32 to 57 per cent (using new cartridges) and could be augmented to a cumulative removal of 88 per cent by three repeated passages of the same water through the filter. On filter cartridges which have reached the half-life recommended by the manufacturer, performance for extracellular microcystin-LR dropped for two of the three brands tested, in one case down to 15 per cent elimination. The study draws attention to the possibility of lysis of cells retained on the filter. It also highlights the need for further development of domestic jug filters if they are to be suitable for microcystin removal. In addition, the study emphasises the need for evaluation of performance of treatment processes in specific situations, particularly if scaled down for domestic use.

Other approaches for individual households and small communities involve methods of filtration, activated carbon and oxidation. As for large-scale plants, slow sand filtration will be effective in removal of cells, and will probably contribute to removal of dissolved cyanotoxins. Rapid blocking can be avoided by pre-treatment to control turbidity or by management of flow regime. Bankside filtration could also be effective and applicable to small community supplies. Addition of chlorine to filtered water at a dose high enough to oxidise microcystins has already been discussed with respect to the benefits for microcystin removal in relation to the problems of by-product production at high DOC levels.

Household treatment approaches have the problem of assessment of performance and quality control. Furthermore, they may enhance social differences, if they are available only to those who can afford them rather than providing "health for all".

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