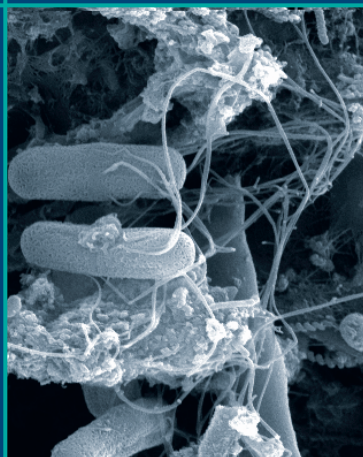
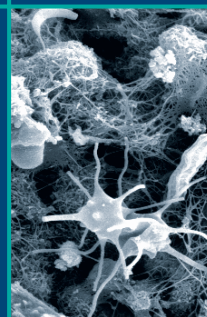


The Cooperative Research Centre for

Water Quality and Treatment



Biological Filtration, Ozone and Activated Carbon



Occasional Paper

9

BIOLOGICAL FILTRATION, OZONE AND ACTIVATED CARBON

CITY WEST CAMPUS, UNIVERSITY OF SOUTH AUSTRALIA

18 NOVEMBER 2003

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Public Health Aspects Of Rainwater Tanks In Urban Australia
CRC for Water Quality and Treatment Occasional Paper 10

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PREFACE

The Cooperative Research Centre (CRC) for Water Quality and Treatment was established in 1995 to provide a strategic research capacity for the Australian water industry. Its mission statement, drafted at that time, reads “To assist the Australian water industry produce high-quality drinking water at an affordable price”. Its brief has expanded since then to encompass such issues as sustainable water sources and more recently has included a portfolio of strategic wastewater issues.

The key measure of success for the CRC for Water Quality and Treatment is to have the knowledge gained from its research programs converted into practical solutions and management practices and used by the Australian water industry.

Take-up of new knowledge occurs in many ways. Having the potential users of such knowledge intimately involved in the development and implementation of the research programs certainly facilitates this process.

As one means of promoting the uptake of new knowledge, the CRC also conducts technology transfer workshops with CRC industry parties and other collaborators. It also publishes the results of its work in a variety of ways. Its Occasional Paper series is one of those ways.

INTRODUCTION

This Occasional Paper is the result of a technology transfer workshop organised by the CRC for Water Quality and Treatment and held at the University of South Australia on 18 November 2003. This workshop, **Ozone, Biological Filtration, and Activated Carbon**, presented some of the outcomes of research within the CRC's Water Treatment Technology program.

While the combination of ozone and granular activated carbon has been widely adopted in drinking water plants in Europe and the United States for over a decade, Australia is relatively recently turning to these processes for the production of palatable, safe drinking water. Internationally the focus has been mainly on the removal of industrial and agricultural pollutants, as well as minimising disinfection by-products by reducing dissolved organic carbon (DOC). The removal of DOC is also an important factor for Australian water authorities, but probably the greatest concerns are the removal of tastes and odours and toxic compounds produced by cyanobacteria.

The CRC has an established research record in the area of activated carbon adsorption, and recently much work has been undertaken on the investigation of ozonation and biological filtration for the removal of these problem compounds. It is also recognised that the full scale treatment facilities already utilising these processes have valuable operational and research information to share with those utilities considering the investment in more advanced treatment processes.

A major focus of the **Ozone, Biological Filtration, and Activated Carbon** workshop was the identification and discussion of the problematic issues faced by the water industry in the application of these techniques. Issues to be discussed were requested through a CRC email list in advance of the workshop. There was an excellent response, and enough discussion topics were introduced to the workshop to generate a lively and informative debate. In addition, experts in these fields from research centres, universities and industry were invited to participate by making a brief presentation about the major findings of their investigations into the application of these techniques and contributing to the discussions focussed on these issues. Overall the workshop was a great success, due to the enthusiasm of the participants, and their willingness to share their experiences and knowledge.

This occasional paper presents a series of articles contributed by the experts invited to give presentations during the workshop. These papers summarise the important issues facing water authorities in Australia, and the way in which activated carbon, ozone and biological filtration can be utilised to overcome these problems.

A transcript of the discussions that occurred as part of the workshop can be obtained from the workshop convener and senior research scientist at the Australian Water Quality Centre, Dr Gayle Newcombe.

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AN ASSESSMENT OF THE BENEFITS AFFORDED BY THE CONTINUOUS VERSUS INTERMITTENT OPERATION OF OZONE FOR DRINKING WATER TREATMENT

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ABSTRACT

Stricter regulation by the Office of Water Services (OFWAT), United Kingdom, has encouraged water companies to optimise all stages of the water treatment process. This work reviews the ozonation process, in order to evaluate the benefits and disadvantages of continuous versus intermittent ozone operation.

Two advanced water treatment works (AWTW) were surveyed, Farmoor AWTW, which involves traditional (chemical) treatment processes, and Kempton Park AWTW, which incorporates slow sand filter Sandwich™ beds. Both reviews indicated that continuous ozone operation would result in an optimised solution based on dependability of ozone plant, reliability of water quality and cost efficiency.

INTRODUCTION

Stricter regulation by OFWAT has encouraged all water companies to continually review and optimise their OPEX costs. In addition, new legislation puts increasing demands on existing technology, forcing the water industry to continually seek more economically efficient and reliable treatment processes.

Such was the case with the introduction of the new Water Supply (Water Quality) Regulations in 1989, which stated that pesticide concentrations leaving a water treatment works should be less than 0.1 µg/l for any individual pesticide and less than 0.5 µg/l for total pesticide concentrations (Water Supply Regulations, 1989). As a point of comparison, it has been estimated that one drop of isoproturon can contain up to 500,000 µg of the active ingredient (Carter, 2001). In order to achieve the standards set in the new Water Quality Regulations, Thames Water developed the advanced water treatment (AWT) program. This involved different combinations of ozone (a strong oxidising agent) and granular activated carbon (GAC - an adsorption medium). All GAC used in Thames Water is Chemviron Carbon F400 grade carbon, except for one groundwater site which uses FI00 grade, predominantly for solvent removal.

Ozone and GAC have been installed at all large surface WTWs, whilst groundwater WTWs deemed to be at risk from pesticides have GAC units only. At surface WTWs

the GAC was either installed in stand-alone vessels or incorporated into the SSFs (referred to as the GAC Sandwich™). Ozone, relative to conventional treatment, is an expensive process. However, the question posed was whether continuous operation of ozone was essential and what were the implications of operating with periods of no ozone.

In order to answer the question a review of operational procedures at two Thames Water surface water treatment works was commissioned. The first treatment works, Farmoor AWTW, is the principle Thames Water treatment works in the Oxford area and involves traditional (chemical) treatment processes. The second site is one of Thames Water's large London treatment works, Kempton Park AWTW, which incorporates slow sand filter (SSF) Sandwich™ beds. The aim of the work was to assess the efficiency, and to compare the benefits, of continual operation of ozone against intermittent operation for water treatment. Particular consideration was paid to the impact on OPEX costs, process reliability and water quality.

SITE DESCRIPTIONS

Kempton Park AWTW

Kempton Park can supply a maximum flow of 160MLD, although the average flow rate through the works is 135MLD. In 1996 ozone was installed at the site. At the same time GAC was installed within the SSF beds, converting the traditional SSF beds into GAC Sandwich™ beds.

Kempton Park AWTW receives its water from the River Thames, which has first passed through one or more bank-side storage reservoirs. A retention time of approximately 90 days allows a degree of settlement before being transported, via aqueduct, to the treatment works. Here the water passes through sand only rapid gravity filters (RGF), which removes the larger solids, including some algae. These filters are periodically backwashed with a combined air/water scour, in order to remove the trapped matter and reduce headloss. After the RGFs the water is ozonated.

Ozone is produced on site by the conversion of liquid oxygen (LOX) into ozone using advanced technology (AT) generators.

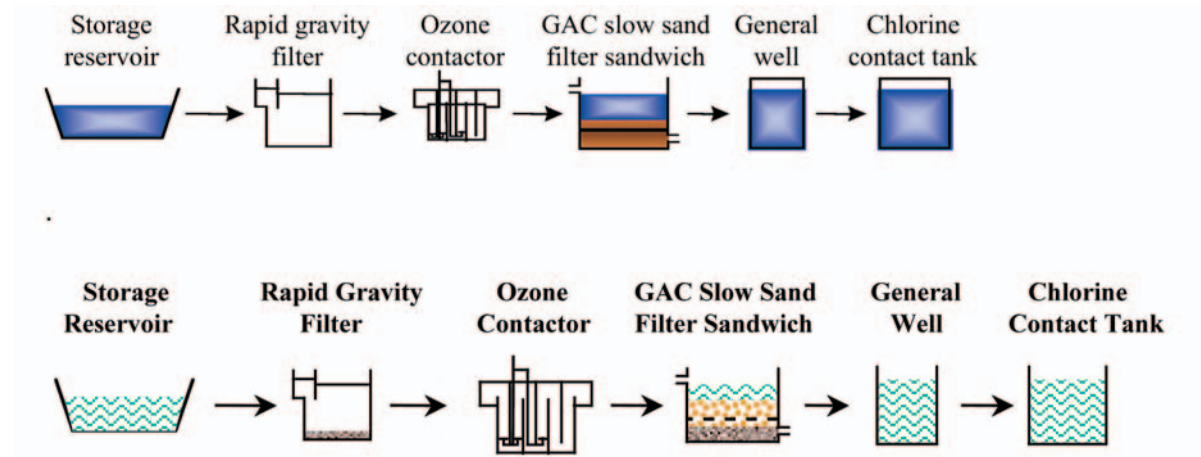


Figure 1 Schematic of Kempton Park AWTW

These generators produce ozone at 9 to 11% (nominally 10% concentration). The ozone is then dispersed through bubble diffusers in the base of the ozone contactors where it is transferred into the water stream. The water, now free of residual ozone, flows through the GAC Sandwich™ beds under gravity, before final chlorination and passing into the distribution network. The treatment process is summarised in Figure 1.

Farmoor AWTW

Advanced water treatment was installed at Farmoor WTW in 1995. Farmoor can supply a maximum of 115MLD, although the average flow rate is 99.5MLD. As at Kempton Park, the water is sourced from the River Thames, which flows into two bank-side storage reservoirs that supply the treatment works. During periods of high algal blooms in the reservoirs, the water can be sourced directly from the river.

The inlet water to the treatment works is split into two streams. Both streams go first to the pre-ozone contactors and then to the coagulant mixer tanks where polyaluminium chloride is dosed. After coagulant dosing, the majority of the flow (90MLD) goes onto

dissolved air flotation (DAF), with the remainder going through upflow precipitators. The streams then combine and pass through sand only RGFs before main ozone contactors and GAC adsorption. The final stage involves microstrainers, pH adjustment and chlorination. A schematic of the treatment works is given in Figure 2.

MATERIALS AND METHODS

This work involved the review of historical data. Data were collected from many sources within Thames Water, including past research data, data downloaded from site operational software (Surveillance Collection And Data Acquisition: SCADA) and operational and statutory laboratory data. These data allowed an assessment of the impact of ozone being 'on' or 'off' on process efficiency.

Models were set up and used to assess the impact of ozone use on four different process areas:

- Ozone generation
- Secondary treatment
- GAC reactivation
- Disinfection

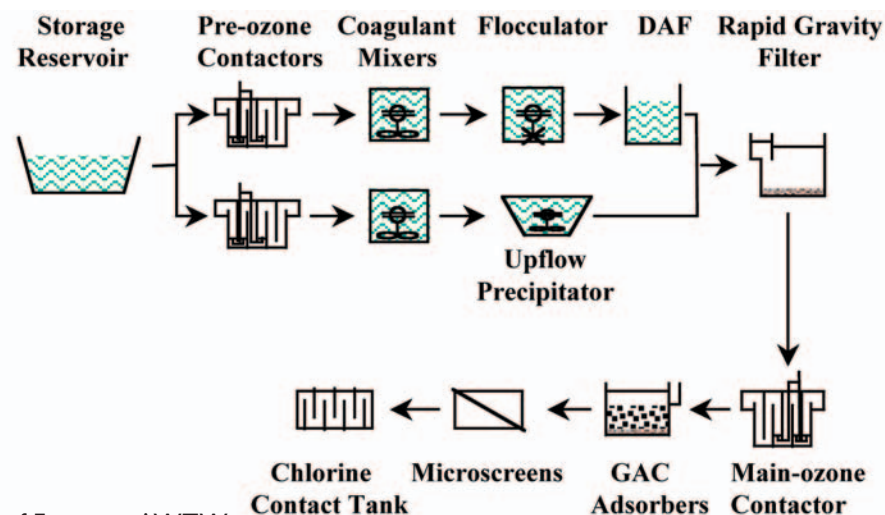


Figure 2 Schematic of Farmoor AWTW

Data from Kempton Park AWTW was analysed over the period of one year (July 1999 to June 2000) except for SSF data, which were analysed between the period of January 1997 to June 2000. The GAC Sandwich™ bed data was projected from installation data through to 2020, in order to better assess the long-term benefits of ozone on GAC management. In addition to this work a one-month slot was considered to compare the impact on the treatment process of ozone 'off' (April 2000) to ozone 'on' (June 2000). These months were chosen based on similarities between output flow and final turbidities. In addition, the period chosen to assess ozone 'off' included only six days of the month when the ozone was operating.

As for the work carried out at Kempton Park, the GAC data from Farmoor AWTW were projected from 1st August 2000 to 2020. Power usage and costs were assessed between June and August 2000. The ability to model and predict future trends and process costs at Farmoor was limited. This work reviewed available data without impacting on operational procedures. Due to the operational strategy employed at Farmoor no data was available for periods of no ozone.

In addition, different operational protocols for the GAC resulted in GAC management and cost predictions being unrepresentative and hence have not been included in this paper.

RESULTS

Pesticide Data

AWT was introduced to Kempton Park AWTW and Farmoor AWTW to ensure adequate removal of pesticides and compliance of the 1989 Water Quality regulations. Currently, the pesticide posing the greatest risk throughout the Thames Water catchment is isoproturon. The main threat posed by isoproturon is the high concentrations encountered typically during the winter and spring months. Isoproturon levels at the inlet to Walton AWTW, a London surface water treatment works, is given in Figure 3. This figure gives the number of days during the pesticide season (October to April) when the isoproturon concentration at the inlet to Walton AWTW was recorded greater than 0.1 µg/l, and the estimated total mass of isoproturon recorded during the season.

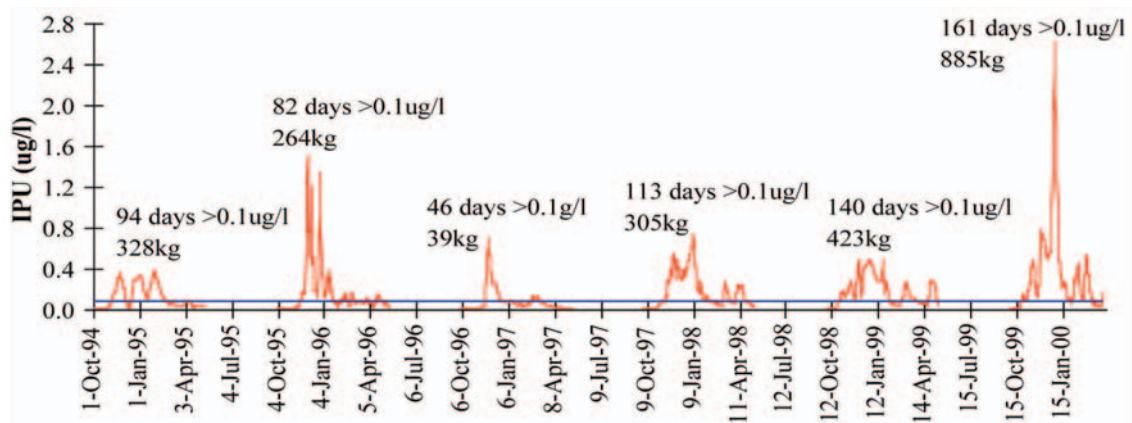


Figure 3 Concentrations of Isoproturon monitored at the inlet to Walton AWTW (October 1994 to May 2000)

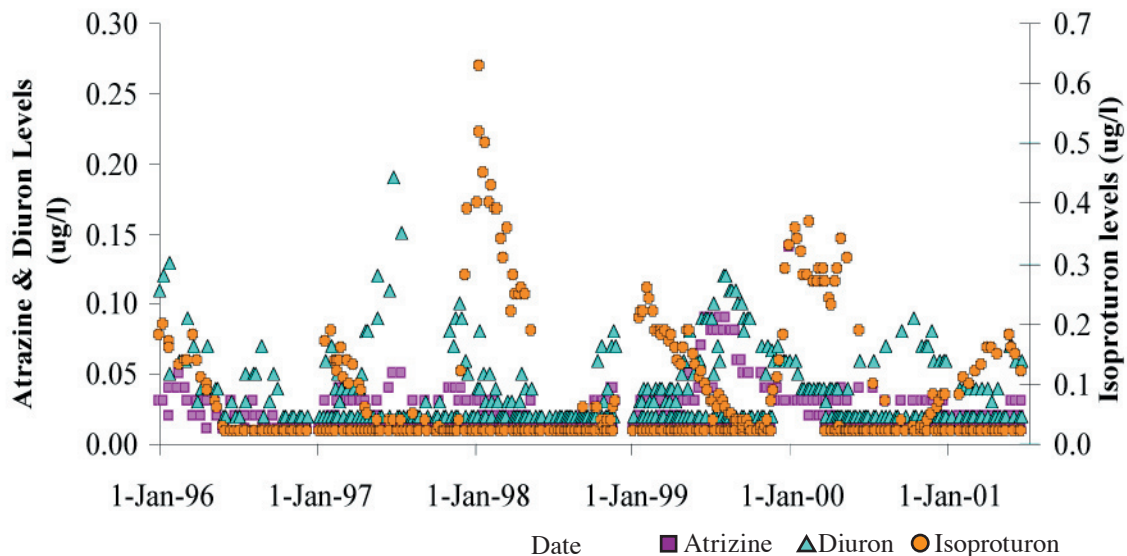


Figure 4 Selected pesticide concentrations at the inlet to Kempton Park AWTW (January 1996 to July 2001)

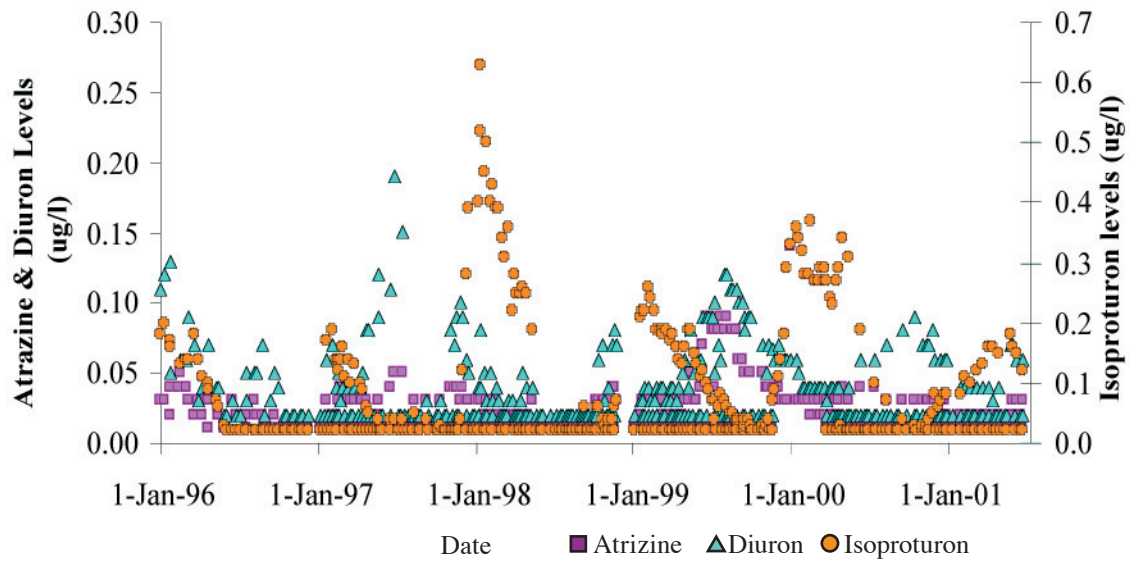


Figure 5 Selected pesticide concentrations at the inlet to Farmoor AWTW (January 1996 to July 2001)

Levels of Isoproturon are similar at the intakes to Kempton Park and Farmoor AWTW, although even higher levels have been recorded (peaks up to $20\mu\text{g/l}$) in a provinces river during November 2001. The provinces region of the Thames Water catchment can also experience significant proportions of phenoxy acids, in particular mecoprop. Although the concentrations of mecoprop are generally considerably less than isoproturon, it is much more resistant to removal, and consequently, lower concentrations are still a reason for concern.

Pesticide concentrations monitored at Kempton Park and Farmoor AWTWs are detailed in Figure 4 and Figure 5 respectively. Weather plays a significant

role in the concentrations of pesticides measured in river courses. A heavy downpour of rain, soon after pesticides have been applied to land, will wash pesticides into river courses, which may be used for abstraction. Such storms may also result in a second application of pesticide being made.

Atrazine and isoproturon removal data across the two treatment works are shown in Figure 6 to Figure 9. Pesticide levels below the detection limit have been represented as $0.001\mu\text{g/l}$ less than the detection limit, i.e. $0.009\mu\text{g/l}$ and $0.019\mu\text{g/l}$ for atrazine and isoproturon respectively. The ozone plant was not running at Kempton Park AWTW for all of the dates given in Figure 6 and Figure 7.

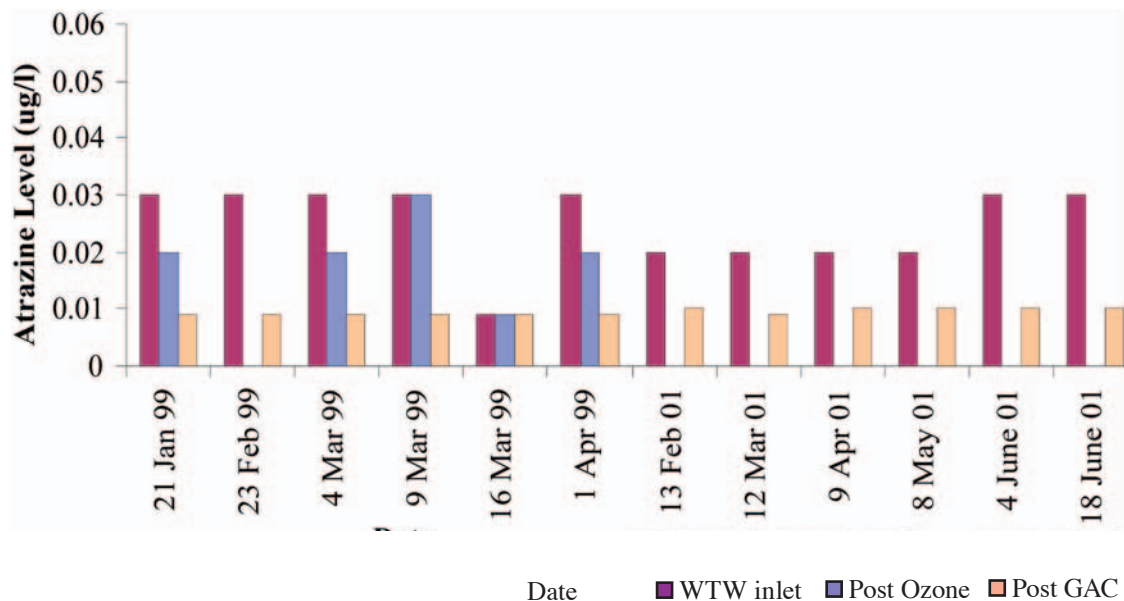


Figure 6 Reduction in atrazine concentrations across the ozonation and slow sand filtration stages at Kempton Park AWTW (January 1999 to June 2000)

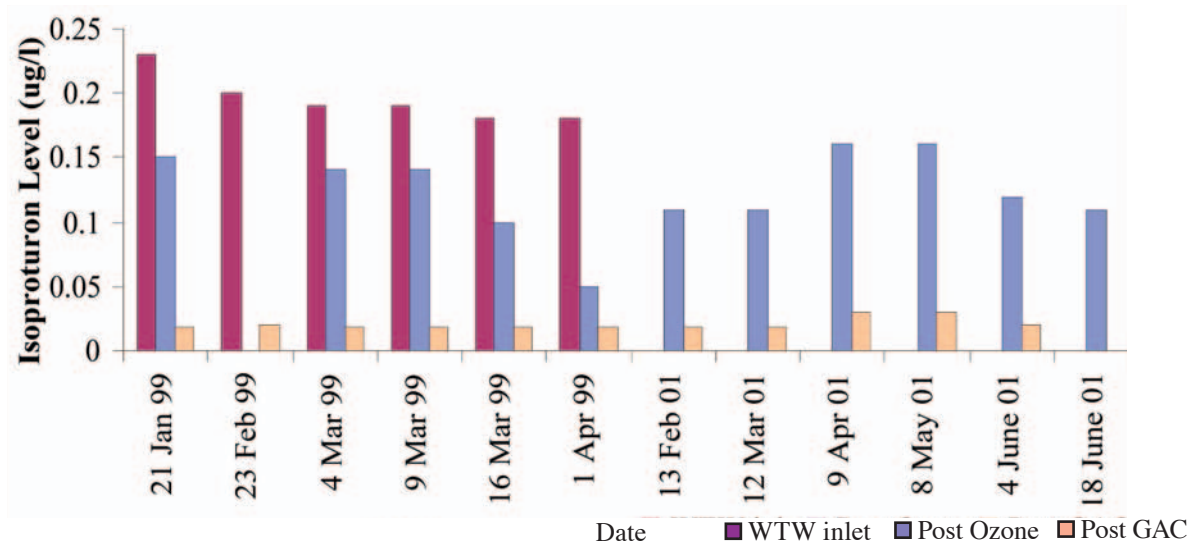


Figure 7 Reduction in isoproturon concentrations across the ozonation and slow sand filtration stages at Kempton Park AWTW (January 1999 to June 2001)

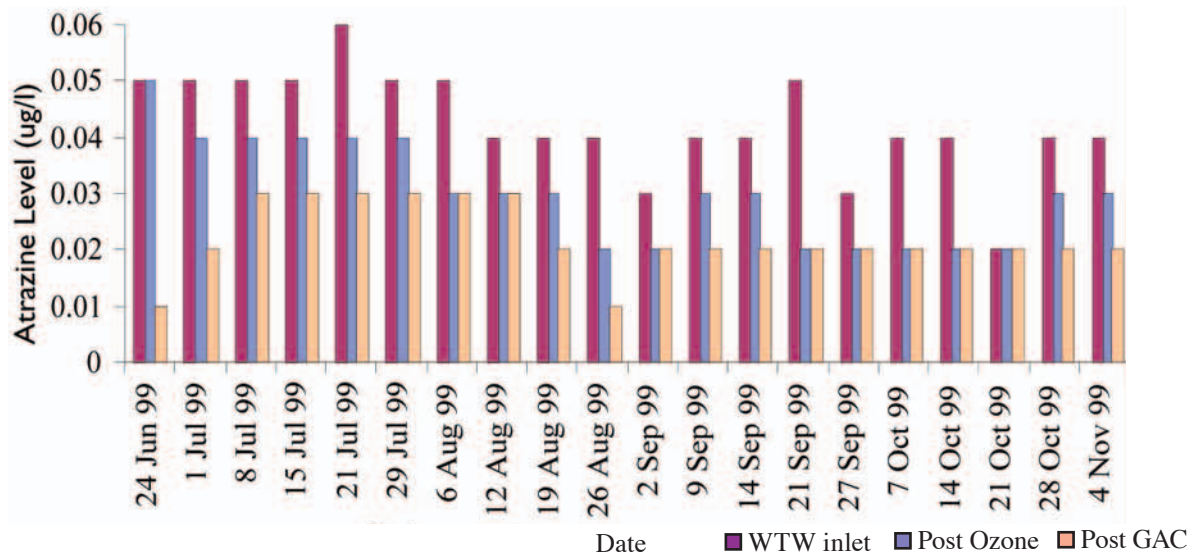


Figure 8 Reduction in atrazine concentrations across the ozonation and GAC stages at Farmoor AWTW (March 1999 to May 2000)

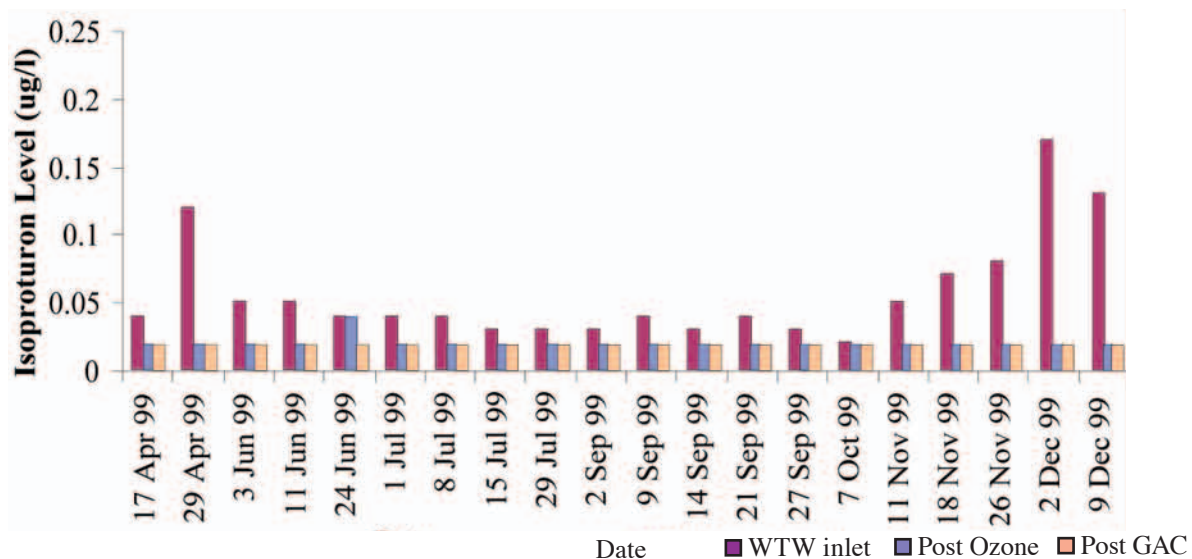


Figure 9 Reduction in isoproturon concentrations across the ozonation and GAC stages at Farmoor AWTW (April 1999 to March 2000)

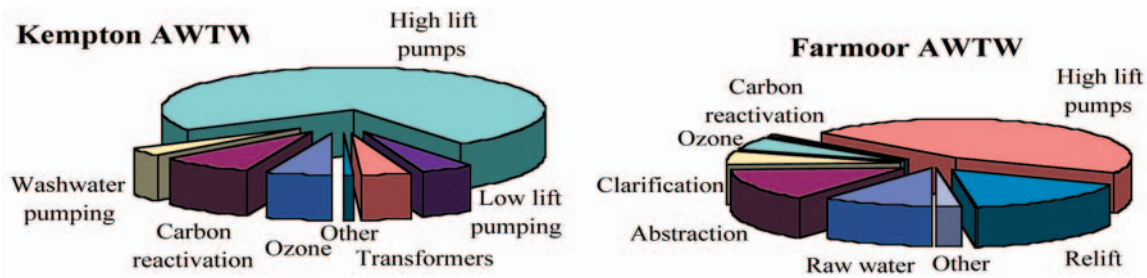


Figure 10 Average power consumption at Kempton Park AWTW (July 1999 to March 2000) and Farmoor AWTW (June 2000 to August 2000)

Ozone generation

The first stage of the AWT process at both Kempton Park AWTW and Farmoor AWTW is ozone. Power and Liquid Oxygen (LOX) are the two main components that contribute to ozone generation costs. The proportional use of power at Kempton Park and Farmoor are detailed in Figure 10. The power data indicate that although ozone is considered an expensive process, it only makes up approximately 5% of total power consumption, with high lift pumps accounting for between 74% (Kempton Park) to 43% (Farmoor). However, the issue under discussion is the need for, and benefit of, continuous ozone operation. Other processes are essential to the treatment process.

As would be expected, the longer the ozone plant was run the greater the power use and LOX consumption. Consequently, average monthly power costs were closely related to the amount of hours the ozone plant was operating. However, although the unit cost of LOX remains constant throughout the year, power costs vary on a half-hourly basis. Electricity prices up to April 2001 generally varied between 2.5p to 15p per KWh. However, changes in the electricity supply market are expected to result in lower average prices. In addition, even when the ozone plant is non-operational, power and LOX are used. Power is used by monitors, lighting and control panels, whilst LOX is vented off to prevent

pressure build-up. This results in an average power plus LOX cost of approximately £26 per day for periods when the ozone plant is shutdown.

Treatment Processes

Kempton Park - Secondary filtration

The second stage of AWT treatment at Kempton Park and Farmoor is via pesticide adsorption onto GAC. At Kempton Park AWTW the GAC is installed as a layer within the SSF beds. The costs associated with SSF Sandwich™ management occur during bed cleaning, resanding and the reactivation and replacement of GAC. SSFs are periodically cleaned (every 2 to 10 weeks) to ensure sufficient flow through the bed. After several cleans the depth of sand above the GAC layer will have been reduced to the minimum depth recommended in the Thames Water SSF Best Operating Practice manual. Consequently, the bed must be 'resanded'. The amount of sand replaced can vary between 200 to 500 mm, depending on the age and quality of the GAC, i.e. if the GAC is soon to be reactivated only a minimum amount of sand will be replaced.

Although all SSFs on an individual WTW share a common inlet, there may be significant hydraulic differences between beds. Flow rates, clean times, headloss can all vary, resulting in great differences between the biological and physical characteristics of the individual beds.

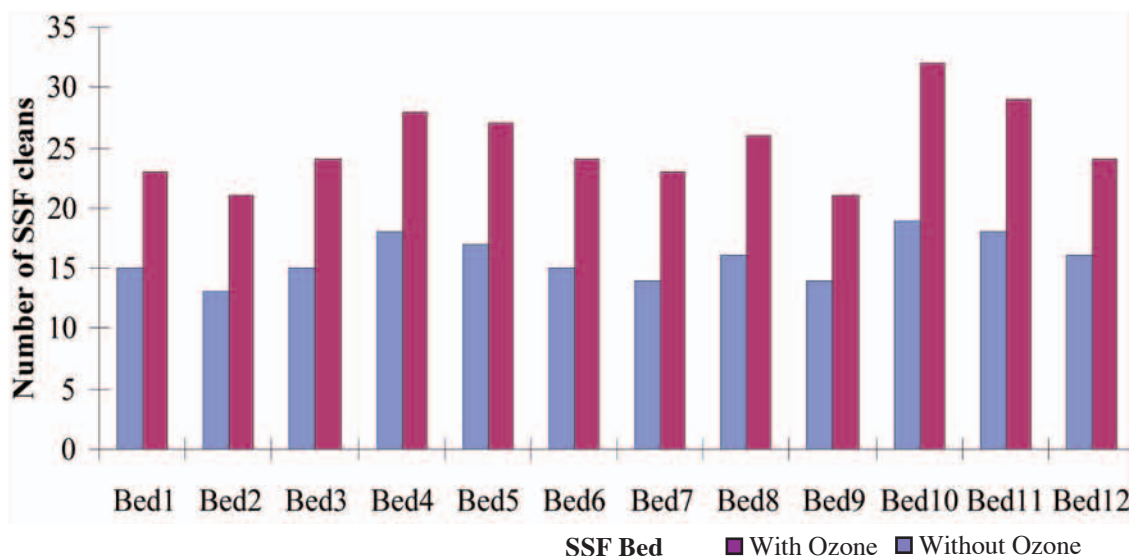


Figure 11 Impact of ozone and no-ozone on SSF cleaning frequency at Kempton Park AWTW (1997 to 2000)

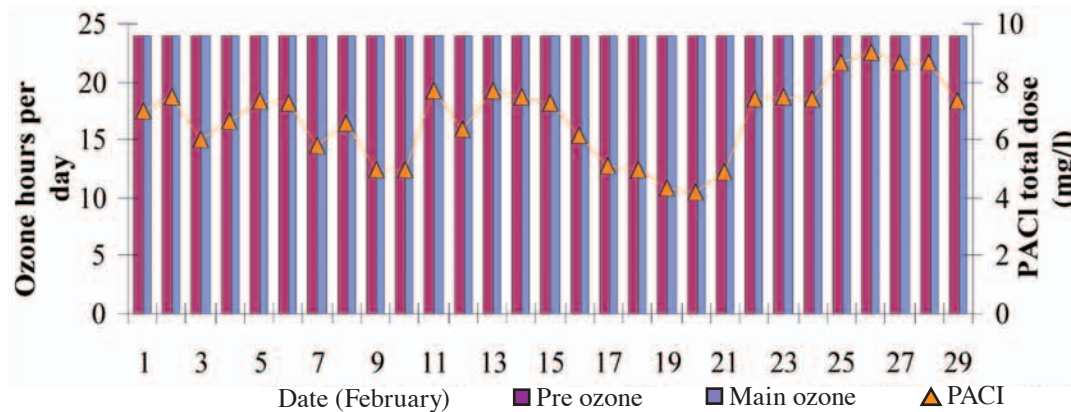


Figure 12 Coagulant dose during continuous pre- and main ozone operation (February 2000)

Site workers estimate that the cleaning frequency of slow sand filters has decreased by 50 to 75% since the introduction of ozone, with a consequent saving in labour and cleaning costs, although algal growth can be a controlling factor during summer months. Figure 11 summarises the impact of ozone on SSF cleaning frequencies at Kempton Park AWTW based on the total number of man-hours employed. The reduction in the number of cleans required per year as a consequence of continuous ozone use has a knock on reduction in the number of resands required. This again has cost saving implications.

Farmoor - Chemical Treatment

Polyaluminium chloride

The main particle removal treatment process at Farmoor AWTW is brought about by chemical coagulation using polyaluminium chloride (PACI). The amount of coagulant dosed is dependent on the flow rate and ozone dose. During high algae bloom periods, the process efficiency can be greatly reduced due to difficulties experienced in the downstream clarification process (precipitators and DAF). Ozone is effective in enhancing the coagulation/flocculation of algae, rendering them easier to remove at later stages of the treatment process.

During low pesticide risk periods, and when there is no algal bloom challenge, main ozone can be turned off at Farmoor. This has little overall impact on the treatment

process. However, during high challenge periods, a loss in ozone can put great strain on other treatment processes, such as DAF and GAC. If the challenge to the works is due to particulate organics, the site operational strategy for responding to short-term ozone loss is to double the coagulant dose. The impact of reduced main and/or pre ozone is detailed in Figure 12 to Figure 14.

Sulphur dioxide and sulphuric acid

Sulphur dioxide and sulphuric acid are used to regulate the residual ozone dose and pH post main ozone, respectively. For maximum efficiency, the main ozone dose should be close to the strategy dose, minimising sulphur dioxide use. Different ozone doses showed no impact on pH. Consequently, the impact of ozone on the use of sulphuric acid is believed to be minimal and will not be included in the cost evaluation of ozone use.

GAC reactivation

GAC is reactivated based on the number of bed volumes treated, where bed volumes is defined as the total volume of water treated divided by the volume of carbon. Certain sites have specific characteristics which need to be taken into consideration (water source, organic loading, process unit design), which may influence the recommended time-in-service. Different reactivation frequencies have been established depending on the GAC type (virgin or reactivated) and ozone operation strategy (continuous or intermittent operation). For

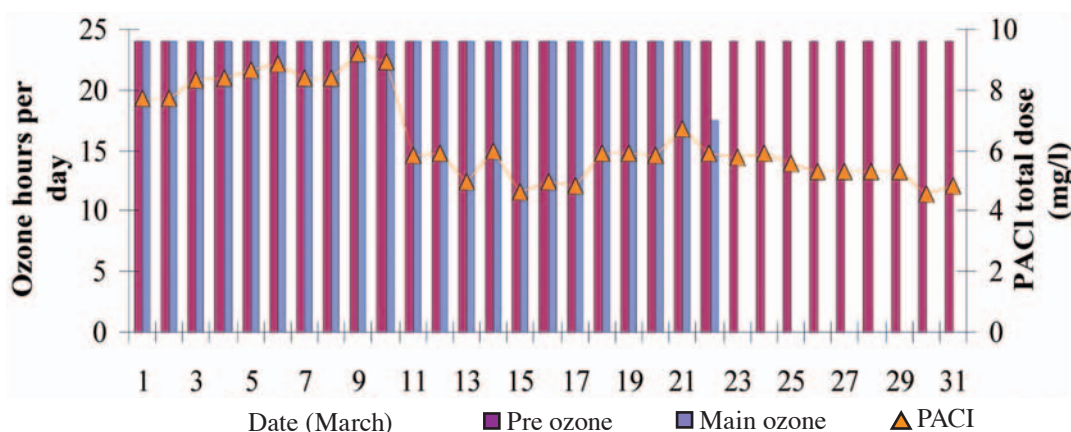


Figure 13 Coagulant dose during continuous pre- and intermittent main ozone operation (March 2000)

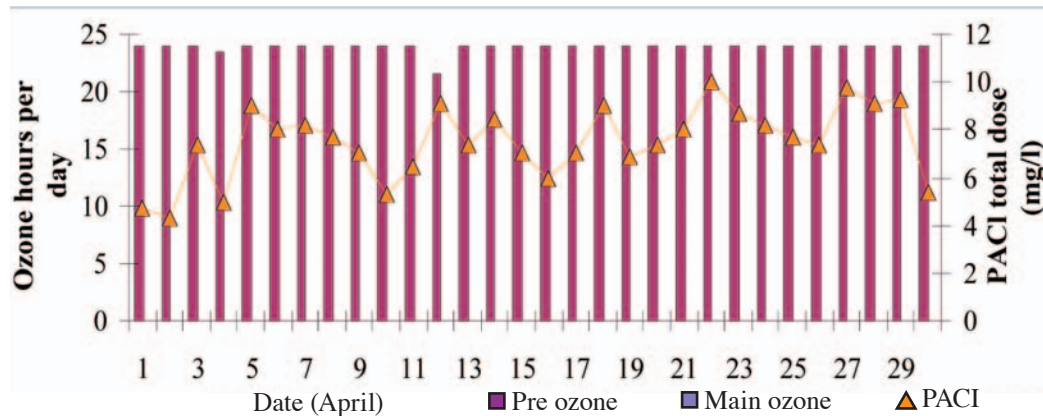


Figure 14 Coagulant dose during continuous pre-ozone operation (April 2000)

the cost evaluation presented in this work, the figures first developed by the Kempton Park Advanced Water Treatment Management Board (TWUL, 1994) have been employed. Although Thames Water does not currently manage its GAC inventory according to these reactivation frequencies, they were based on 10 years research carried out on a 5MLD pilot plant. In addition, the reactivation frequencies allow for a comparison between the operational strategy with ozone on and ozone off to be carried out, and are detailed in Table I.

A model was set up to estimate the GAC management costs under different ozone operation. The model was run for a twenty-year period (2000 to 2020) and assumed a 4% inflation increase each year. It predicted that the bed life of the carbon would be extended by approximately 54% through the continuous operation of ozone (Figure 15).

However, although the model implied that the bed life may be considerably extended, operational factors, such as headloss build up, would have to be taken into consideration. Other work has shown that such operational factors would yield a maximum time in service considerably shorter than that predicted by the GAC model.

The cost of reactivating GAC can be divided into three components, namely reactivation, labour and virgin make-up. The bed life of the carbon will have an obvious impact on the frequency of GAC reactivation, and consequently labour and make-up costs. Make-up is required to replace losses incurred during the removal, separation and reactivation of the carbon. The OPEX costs incurred for GAC management at Kempton Park AWTW are noticeably greater for periods of no ozone, as indicated in Figure 16.

Table I Reactivation frequencies for different carbon types, with and without ozone

GAC type	Reactivation frequency (bed volumes)	
	With ozone	Without ozone
Virgin GAC	88,000	48,000
Reactivated carbon	74,000	40,000
Reactivated carbon (more than one cycle of reactivation)	65,000	35,000

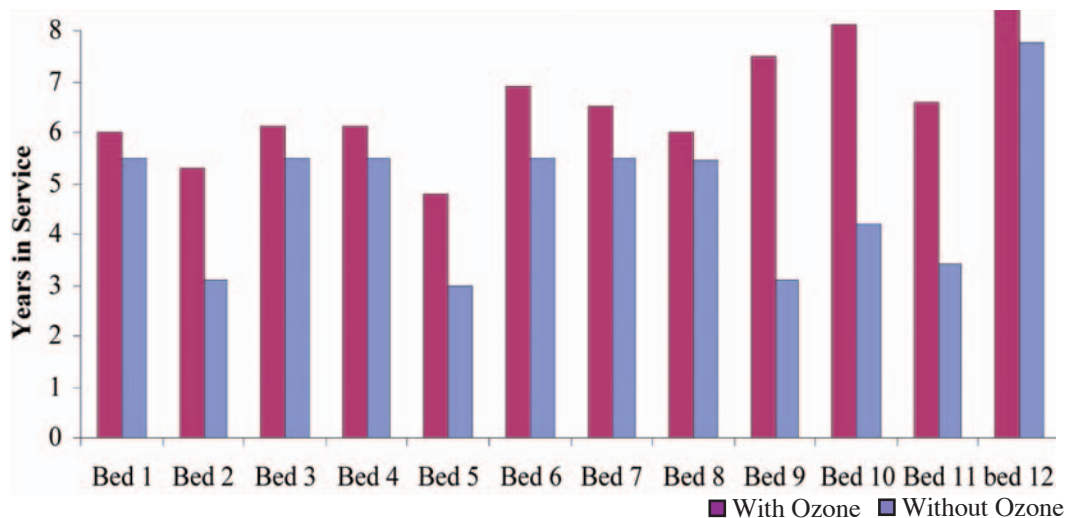


Figure 15 Predicted GAC Sandwich™ bed life at Kempton Park AWTW with and without ozone

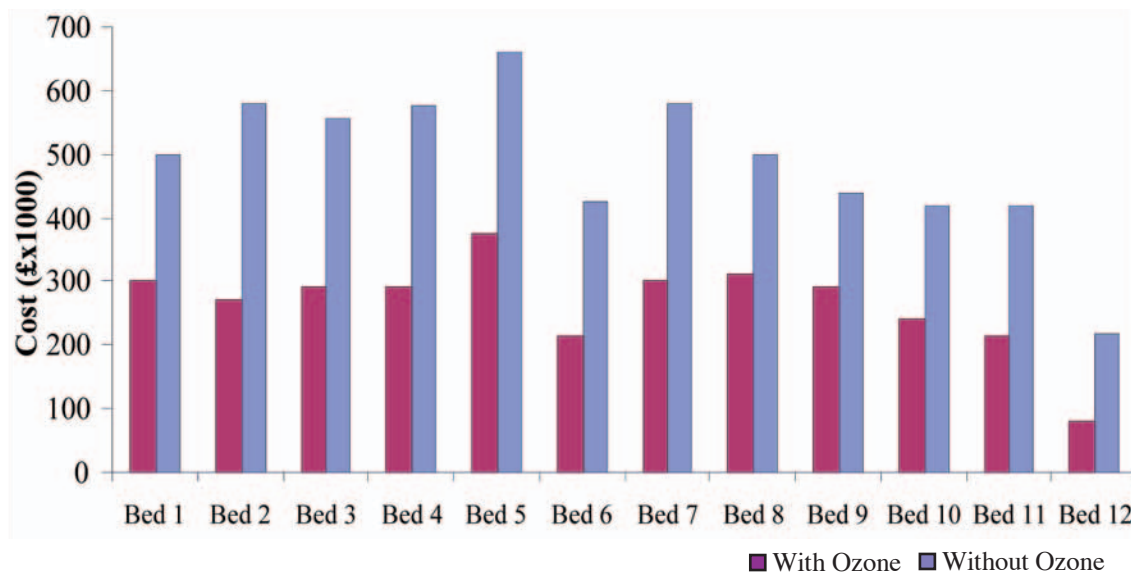


Figure 16 Predicted OPEX for Kempton Park GAC management with and without ozone operation (2000 to 2020)

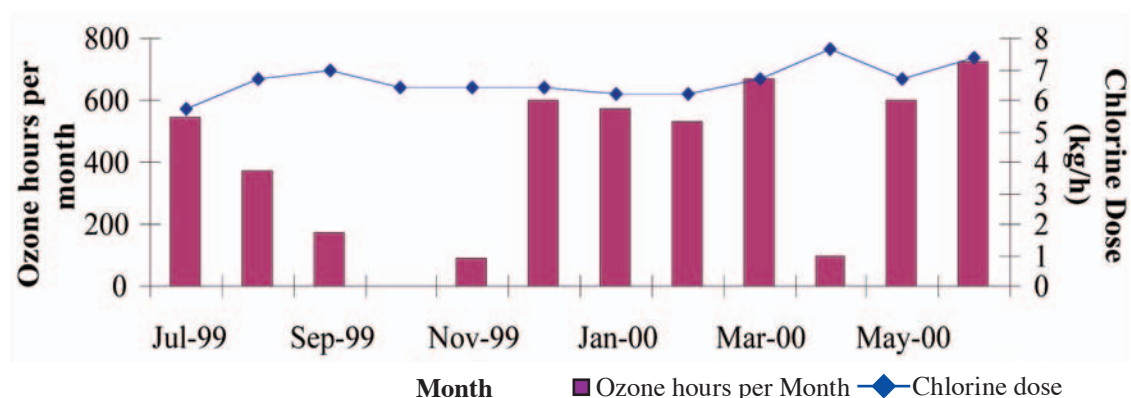


Figure 17 Comparison between ozone use and chlorine demand at Kempton Park AWTW (February to April 2000)

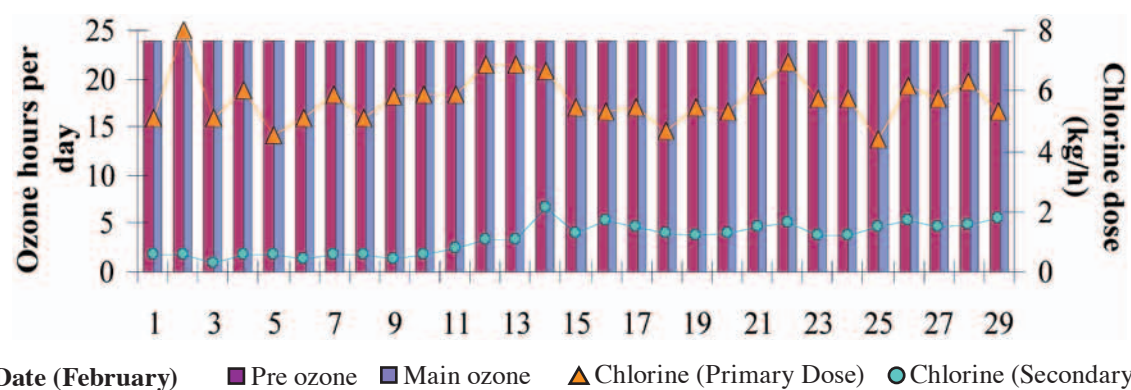


Figure 18 Comparison between ozone use and chlorine demand at Farmoor AWTW (February 2000)

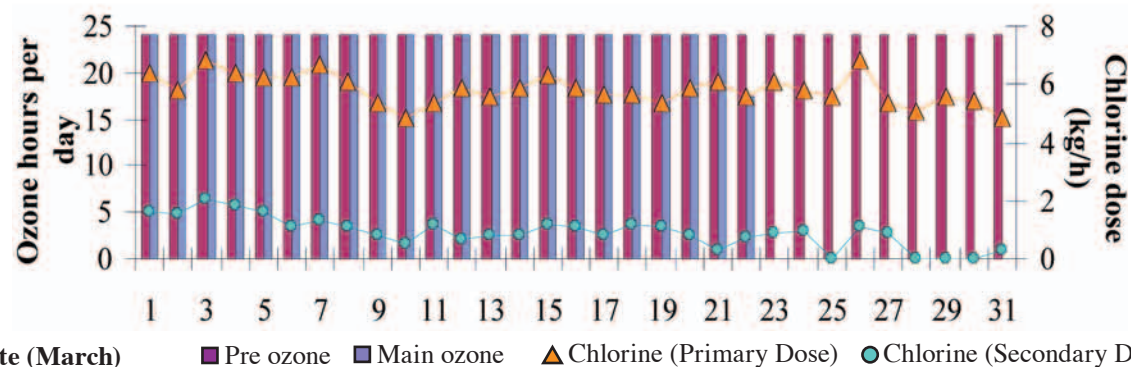


Figure 19 Comparison between ozone use and chlorine demand at Farmoor AWTW (March 2000)

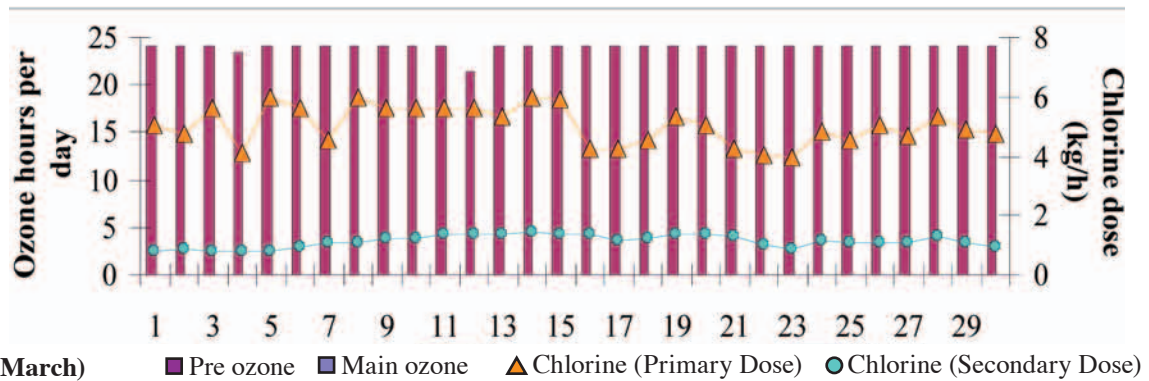


Figure 20 Comparison between ozone use and chlorine demand at Farmoor AWTW (April 2000)

Disinfection

Research into the impact of ozone on disinfection costs found no significant reduction in chlorine demand during continuous ozone operation (Figures 17 to 20). This disagrees with results reported by Hickton (2000).

The discrepancies in the results may be impacted by a time lag between changes in ozone operation and chlorine demand, inlet turbidity and demand output. It is hypothesised that the main reason for the lack of correlation between ozone dose and chlorine demand is due to the GAC acting as the principal process in reducing the total organic loading (TOC) onto the disinfection stage (Bauer et al, 1999). However, it should be noted that ozone assists organic removal and extends the useful GAC life.

Summary of Cost Models

A summary of the process costs associated with continuous and intermittent operation of ozone is given below. The costs at Kempton Park AWTW were easier to predict than at Farmoor AWTW, due to the availability of data when ozone was operational and non-operational. In addition, the impact of ozone operational procedures on GAC management and consequently

SSF run times have been determined, allowing the cost impact of different operational procedures to be assessed (Table 2).

At Farmoor AWTW, no data was available for periods when the ozone was not operational. However, data were available for periods when the main ozone was not dosed, as summarised in Table 3.

GAC management at Farmoor AWTW differs to management at Kempton Park AWTW. The design of the Farmoor GAC vessels allows for the pesticide front to be monitored, allowing longer GAC filter runs without compromising the risk of pesticide breakthrough. Hence basing GAC management cost savings on the reactivation frequencies defined in Table 1 is unrealistic. However, continuous operation of ozone would be expected to extend the service life of GAC.

Table 4 gives an indication of costs that could be incurred if the ozone was turned off, for comparison against continuous ozone operation. These costings have been based on knowledge developed through research over the past decade plus operational experience.

Table 2 Cost predictions for Kempton Park AWTW for periods of operational and non-operational ozone

Kempton Park - £/yr	With ozone	Without ozone
ozone costs =	123,047	90,912
SSF management costs =	18,438	31,154
GAC management costs =	178,119	410,964
	319,605	533,030
Overall saving per year if ozone run continuously =		£193,255

Table 3 Costs for Farmoor AWTW for continuous periods of pre-ozone operational and intermittent periods of main-ozone operation

	Average Pre-Ozone (hours/day)	Average Main-Ozone (hours/day)	Flow to Ozone (Mld)	Average Ozone Cost (£/day)	Average Chemical Costs (£/day)	Average Total Costs (£/day)
February	24	24	106	645	231	876
March	24	17	116	514	238	752
April	24	0	131	239	230	469
May	24	0	96	177	-	-

Table 4 Cost predictions for Farmoor AWTW for periods of operational and non-operational ozone

Kempton Park - £/yr	With ozone	Without ozone
Additional chemical costs =		39,000
Ozone costs =	142,959	
GAC management costs =	163,698	271,287
	306,657	310,287
Overall saving per year if ozone run continuously =		£3,630

DISCUSSION

It is assumed in this paper that ozone and GAC are essential processes to ensure pesticide concentrations in potable water comply with the 1998 Water Supply (Water Quality) Regulations. However, the question posed was whether continuous operation of ozone was essential and what were the implications of operating with periods of no ozone.

One justification for intermittent ozone operation is the risk of bromate formation. Although the details of ozone impact on bromate formation are not in the scope of this paper, it does merit a mention. Past research carried out by Thames Water has demonstrated that at current raw water bromide levels, there is low risk of bromate formation. In addition, during the warmer months, ozone doses are generally reduced since pesticide challenge periods tend to occur in Spring and Autumn months. Consequently, the Thames Water ozone strategy has not been influenced by bromate formation. Consideration may need to be given to the strategy if raw water bromide levels were high and corresponded to high ozone doses.

The two sites chosen for this study represented the traditional (chemical) and the biological (SSF) treatment processes employed by Thames Water for the treatment of potable water. The work highlighted the differences in benefits to be gained from ozonation by different treatment processes. Kempton Park AWTW, which employs biological SSF technology, demonstrated the benefits of continuous operation of ozone, with overall process cost saving of approximately £200,000 per year being achievable with continuous ozone operation. These cost were made primarily through extending the life of GAC and reducing labour costs associated with GAC management.

The benefits afforded by ozone at Farmoor AWTW, were more difficult to evaluate. Data demonstrated that power and chemical costs increased with continuous ozone operation. The savings that would be incurred due to extended GAC bed life and reduced coagulant requirement were difficult to estimate. However, basing costs on operational experience and past research indicated that cost savings would be made. These savings would be less than at Kempton due to lower labour costs required for the managing of the GAC vessels and the longer GAC bed lives achievable due to the design and operation of the GAC vessels.

However, it should be noted that the issues at Farmoor differ greatly to those experienced at Kempton Park. Farmoor is prone to problems associated with algal blooms during the spring and summer months. Ozone enhances the coagulation process, consequently reducing coagulant costs and allowing greater and more reliable water supply to be achieved. The use of ozone at Farmoor has proved necessary not just for pesticide removal, and hence water quality issues, but also to assist in the removal of algae and maintain flows (i.e. to maintain quantity). Without ozone during algal challenge periods, other stages of the process would experience operational difficulties, resulting in increased sludge production, less efficient chemical processes and greater risk to reliable plant output.

The additional benefits of enhanced taste and odour and the reliability of the operational plant must also be considered. In an industry as strictly regulated as the water industry, ensuring that a process is always available during challenge periods is imperative. The operational problems associated with ensuring the reliability of plant only running for 6 months of the year needs to be considered. Maintenance would need to be carried out on the plant in order to ensure availability at all times. The increased difficulty in ensuring 100% availability of the plant adds credence to the recommendation that ozone should be continuously operated.

CONCLUSIONS

This work has highlighted the additional benefits afforded by the continuous operation of ozone. The assessment carried out on Kempton Park AWTW, demonstrated the cost savings that could be achieved at a biological treatment works through enhanced GAC management with upstream ozonation. In addition, traditional (chemical) treatment works such as Farmoor AWTW, can benefit from reduced chemical usage and enhanced process efficiency, ensuring reliable water quality and supply throughout the year.

It is obvious, however, that the cost effectiveness of continuous ozone operation is site specific. Without the algal loadings at Farmoor it may prove more cost effective to operate ozone intermittently. However, additional benefits should not be ignored, such as improved taste and odour and the reliability of operation of the ozone plant.

REFERENCES

- Bauer M, Goodman N, Holmes M, Rachwal A, Shurrock J and Ta T (1999) Advanced Water Treatment Strategy for Control of Pesticides and Disinfection By-Products in London's Water Supply. *14th International Ozone Conference*, 23-26 August, Dearborn. USA.
- Carter A (2001) How do pesticides get to water – The Cherwell Project. Proceedings of the 2001 CIWEM and Pesticide Action Network UK joint conference 'Keeping Pesticides out of Water,' Scientific Societies Lecture Theatre, 7 February, Central London.
- Hickton M (2000) *Personal Communication*, Ozonia Ltd.
- Luckman I (2000) *Assessing the benefits of Ozone use in Chemical Water Treatment*. MSc Thesis, Imperial College of Science, Technology and Medicine, University of London.
- Page M (2000) *Assessing the benefits of Ozone in Biological Water Treatment*. MSc Thesis, Imperial College of Science, Technology and Medicine, University of London.
- Water Supply (Water Quality) Regulations (1989) Statutory Instrument 1989 No 1147, Water England and Wales. HM Stationery Office, London.

THE ROLE OF OZONE IN IMPROVING DRINKING WATER QUALITY IN LONDON AND OXFORD

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ABSTRACT

In recent years, drinking water quality has become a major subject for public and political debate, with the issue of pesticides in drinking water receiving much attention. The EC Drinking Water Directive included a limit of 0.1 µg/l for individual pesticides, a standard far more stringent than health-based minimum levels set by such bodies as the World Health Organization and the US Environmental Protection Agency.

With traditional treatment processes such as chemical coagulation, flocculation, filtration and slow sand filtration unable to meet the stricter pesticide standard, an additional method of treatment was required. Consequently, ozone and granular activated carbon (GAC) have been installed at all the major water treatment works (WTWs) in London and Oxford treating River Thames water. Groundwater WTWs, deemed to be at risk from pesticides, have GAC filters only.

Computational Fluid Dynamics (CFD) was investigated as a tool for optimising the design of ozone contactors. The aim was to distribute ozone flow uniformly so that maximum contact would be made between the water and gas. However, the application of ozone in water treatment processes remains expensive when compared to conventional treatment. Consequently, a cost benefit analysis of continuous versus intermittent ozone operation was carried out. Operational data was obtained and compared for two Thames Water UK and Ireland (TWUKI) surface water treatment works (one conventional (chemical) works and the second based on biological processes).

INTRODUCTION

Thames Water UK and Ireland (TWUKI) treats approximately 2800 MLD of water, primarily originating from the lowland rivers Thames and Lee. This water supplies over 7.8 million customers, principally in London and Oxford. Traditionally London water treatment consisted of intake management (pumping water from the rivers), storage for 30 to 80 days in deep reservoirs, filtration through rapid gravity (RGF) and slow sand filters (SSF) and final chlorine disinfection,

with a chloramine residual maintained in distribution (Toms, 1987).

More recently, strategies have been employed to uprate the supply and improve the quality of treated drinking water. The first strategy was required in order to meet the demands of the Thames Tunnel Ring Main, which supplies London with treated water (Glendinning & Mitchell, 1996). This required the modernisation and hydraulic uprating of the major river-derived water treatment works. The second strategy was required to address the EC Drinking Water Directive (EC 1980) and the UK Water Supply (Water Quality) Regulations (No. 1147, 1989), principally to achieve the 0.1 µg/l pesticide standard (0.5 µg/l for total pesticides). This has resulted in the implementation of advanced water treatment (AWT) in the form of ozone and granular activated carbon (GAC) at all the major water treatment works. For most pesticides this 0.1 µg/l standard is far more stringent than health-based standards set by such bodies as the World Health Organization and the US Environmental Protection Agency.

Considerable research has been undertaken into the design, operation and optimisation of advanced water treatment (AWT) in TWUKI over the past decade (Rachwal *et al*, 1988; Foster *et al*, 1991a; Foster *et al*, 1991b; Rachwal *et al*, 1992; Rachwal *et al*, 1993; Bauer *et al*, 1994; Shurrock *et al*, 1988). TWUKI has concluded that the use of GAC, either alone or in conjunction with ozone, represents the best available technology for pesticide and organics control. The design, performance and optimisation of the ozone plants included the development of computational fluid dynamic (CFD) models. This assisted in determining the parameters, which lead to uniform flow distribution over the volume of the contactor. Such flow conditions maximise the contact between the water and gas, allowing for optimum mass transfer of ozone into the water stream.

Design Development

In order to determine the optimum operational process and management strategy for organics removal a 5MLD pilot plant was built, using the same source water that supplied the operational works. The plant consisted of two parallel streams, each with two-stage ozonation, rapid gravity filtration, GAC adsorption and slow sand

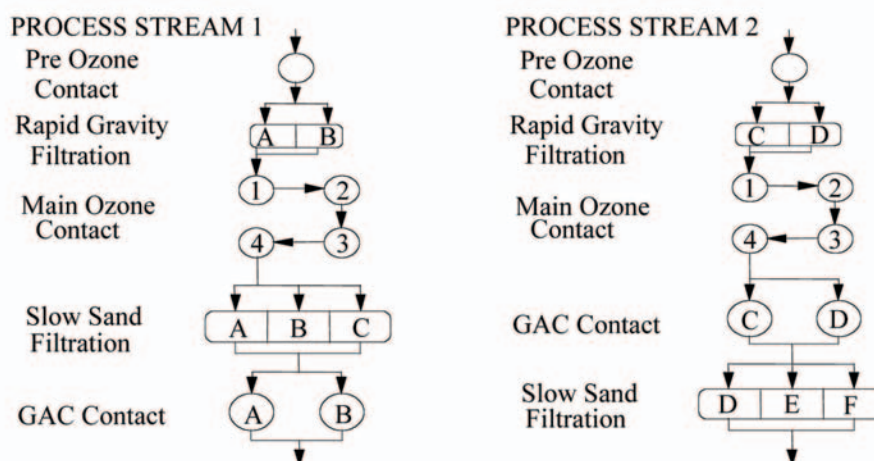


Figure 1 Advanced water treatment research plant process design

filtration (Figure 1). Each process stream had four main ozone contactors, with each contactor having three horizontal ceramic diffusers, the central diffusers (the largest) being used most frequently, giving contact times of approximately 15 minutes. Main ozonation was dosed in order to obtain a pre-defined ozone residual, with ozone doses between 1 to 2.7 mg/l giving residuals of 0.1 to 0.35 mg/l and doses between 2 to 4.5 mg/l giving residuals of 0.2 to 0.65 mg/l.

The results from the pilot plant (Table 1) indicated that ozone was less effective for pesticide removal than others papers have demonstrated (Bourgine *et al*, 1997; Meijers *et al*, 1993b). Bourguine *et al* (1997) achieved pesticide reductions of 98% for isoproturon (IPU) and 73% for diuron, when dosed with 2 to 3 mg/l ozone, whilst Meijers *et al*. (1993) reported 98% IPU and 92% diuron removal with 2 mg/l ozone.

The main reason for the lower percentage removal values found by this research is thought to be due to the scale of the experiments. Most of the published work was based on controlled conditions with short-term bench scale experiments. In contrast, the Thames Water research was carried out at large scale, using

the same source water as the operational works, which consequently took into consideration the impact of background organics that may compete with the monitored pesticides. Hence, the Thames Water pilot plant was representative of an operational works, and was subjected to a wide range of environmental variations.

Operational Plant Design

The major challenge facing TWUKI, with regards to organics removal, is from IPU. Figure 2 indicates the levels of IPU recorded in the river for the period of 1995 to 2000. With more precise measuring methods, greater concentrations have been recorder, with a peak of 20 µg/l measured in a provinces river during November 2001.

In order to address the issue of pesticides in raw water AWT processes are in service at all TWUL surface water treatment works. In general, London surface water treatment works are based upon SSF while provinces works follow a chemical coagulation process (Figure 3). A combined ozone and GAC process has been installed at nine of TWUKI's surface WTW, with a further three surface WTW and twenty-one groundwater works having GAC alone. Variations exist

Table 1 Percentage Pesticide Removal at Specific Ozone Doses

Ozone Dose (mg/l)	Diuron		Isoproturon		Atrazine		Mecoprop	
	Range	Average	Range	Average	Range	Average	Range	Average
0.5	0 - 90	32	0 - 90	45			0 - 20	9
1	5 - 90	50	10 - 90	62	0 - 50	15	0 - 80	35
1.5	10 - 90	61	50 - 95	73	0 - 50	25	40 - 85	50
2	60 - 90	68	70 - 95	80	5 - 60	32	50 - 85	61
2.5	60 - 90	74	70 - 95	85	20 - 60	37	50 - 90	69
3	60 - 90	79	75 - 95	90	25 - 70	42	50 - 90	76
3.5	65 - 95	83	75 - 95	94	25 - 70	46	65 - 90	82
4	70 - 95	87	75 - 95	97	40 - 70	49	75 - 90	87
4.5		90		99	52			91
5		92			54			95

Note: For samples where the pesticide concentration was below the detection limit, percentage reductions were calculated with the assumption that the minimum pesticide concentration was 0.1 µg/l or 0.2 µg/l, depending on the detection limit for the particular pesticide.

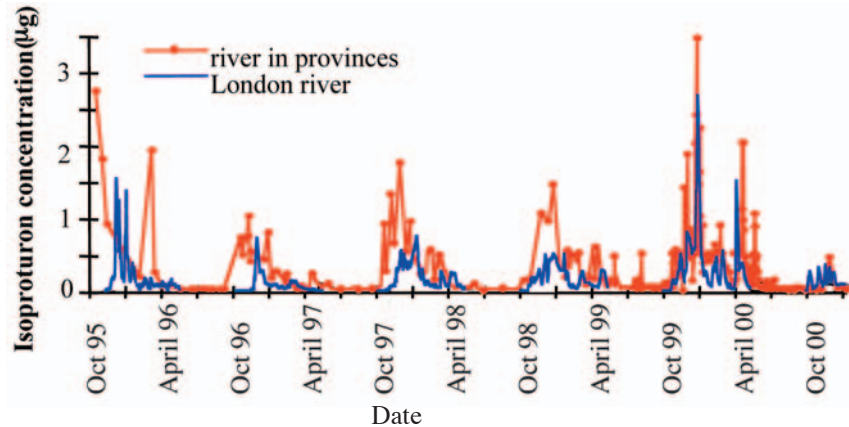


Figure 2 Isoproturon concentration in river (1995 – 2000)

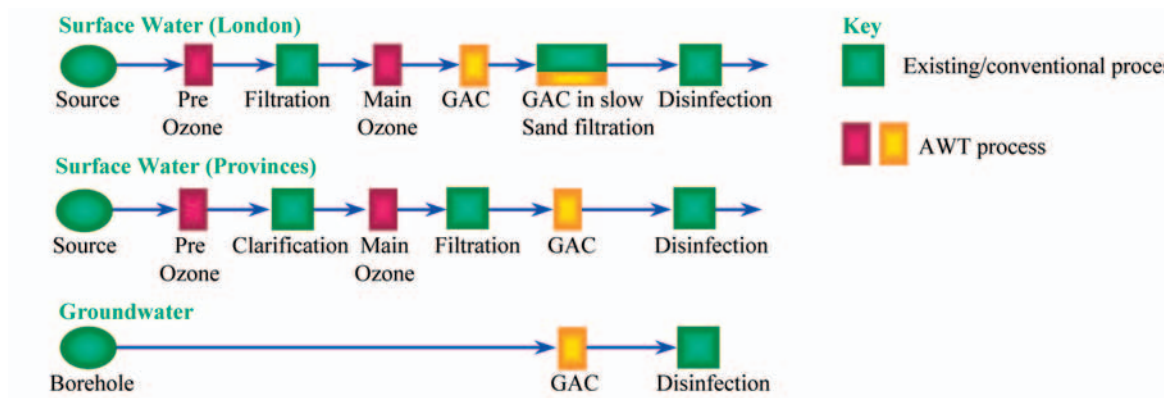


Figure 3 Schematic of GAC and ozone at surface and groundwater sites

in the design of AWT processes for ozone and GAC, as indicated in Table 2. The ozone generators used by TWUL are either Ozonia Conventional Technology (CT) or Advanced Technology (AT) generators producing ozone at 6% and 9 to 11% (nominally 10% concentration), respectively. Ozone and oxygen design data for the nine surface water treatment plants is shown in Table 2.

Computational Fluid Dynamics

CFD was used as a design tool, and calibrated using a perspex model of an under/over baffle tank, with an air nozzle after the second baffle for co-current flow and after the third for counter-current flow. Detailed measurements and CFD simulation are presented elsewhere (Ta & Hague, 2001).

Table 2 Design ozone and oxygen capacity for major sites

WTW	Average daily flow * (Ml/d)	Raw water supply (catchment / type)	Ozone		Max Ozone Dose (mg/l)	Peak Ozone Capacity (Kg/h)	Peak Oxygen Demand	
			Pre	Main			(Tonnes/day)	(kg/h)
Site 1	690	LT/res	yes	yes	5.0	146	24.9	(1037.5)
Site 2	680	LT/L/res	no	yes	5.0	143	24	(1000)
Site 3	690	LT/res	yes	yes	3.5	116	27.9	(1162.5)
Site 4	200	LT/res	no	yes	4.5	43	7.9	(329)
Site 5	200	LT/res	yes	yes	5.0	43	12.5	(521)
Site 6	73	MT/dir	yes	yes	5.0	16	4.5	(187.5)
Site 7	109	UT/res	yes	yes	5.0	23	6.7	(279)
Site 8	38	UT/res	yes	no	5.0	14	2.2	(92)
Site 9	21	C/res	yes	yes	5.0	4.5	1.3	(54)

Key to Surface Water Supply Catchment

* Sustainable flows for March 1999; LT: lower Thames MT: middle Thames UT: upper Thames WE: river Wey L: river Lee C: river Cherwell T: river Tillingbourne W: Windrush

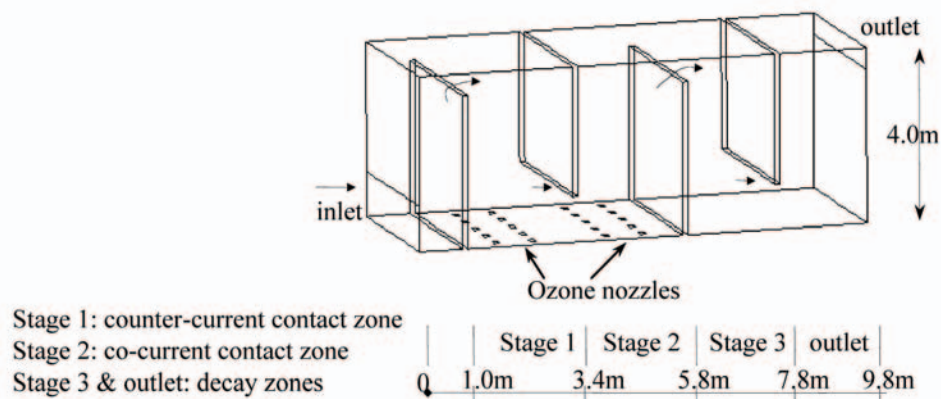


Figure 4 Multi-compartment ozone contactor

Figure 4 shows a typical multi-compartment ozone contactor. In the contact zones (stages 1 & 2) a mixing condition is required for mass transfer, while in the decay stage (3 & outlet) plug flow conditions are required to achieve sufficient residence time. To ensure even gas concentration across the model, the nozzle spacing was found to be at least 0.8m for 0.5mm gas bubbles size.

Figure 5 shows the velocity vectors for the water phase and the gas concentration contours. The flow rate was set at $0.12\text{m}^3/\text{s}$. In stage 1, water and gas were counter-current, giving rise to vertical circulation and mixed flow conditions. The short-circuiting flow path was observed to be downward, hugging the flow-over baffle, and then along the bottom of the tank. The gas concentration was higher in the region close to the flow-under baffle. For design calculations, the gas concentration must be set to that along the preferential water flow path.

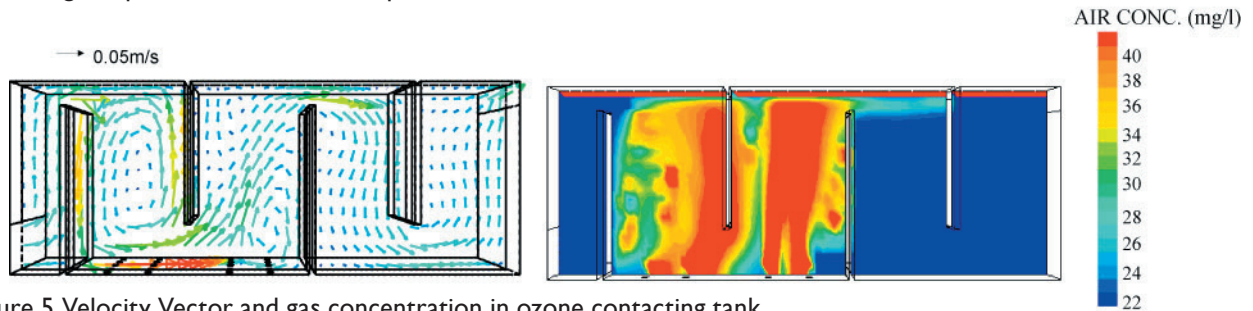


Figure 5 Velocity Vector and gas concentration in ozone contacting tank

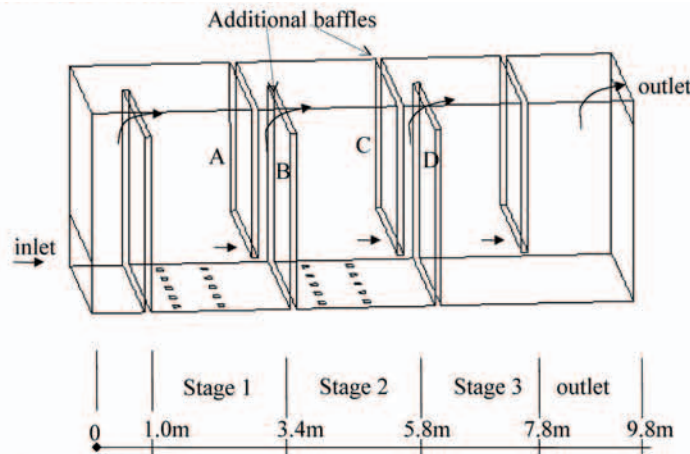


Figure 6 Multi-compartment ozone contact tank with additional baffles

Figure 6 shows another configuration of a multi-compartment ozone contactor. This includes 2 additional baffles. Both stages 1 and 2 were then counter-current flow. The dimensions of all stages, as well as flow conditions, were kept the same as in the previous example.

The velocity vector and gas concentration is shown in Figure 7. In the region between baffles A and B in stage 1, high gas concentration was observed. This option was therefore considered as a significant improvement. In stage 2, the flow was mixed rather than plug flow. In comparison with the previous un-baffled example, this option was preferable in terms of mass transfer of ozone gas. Stages 3 and 4 were similar to the previous example. Other baffle configurations were assessed but did not give beneficial mixing conditions.

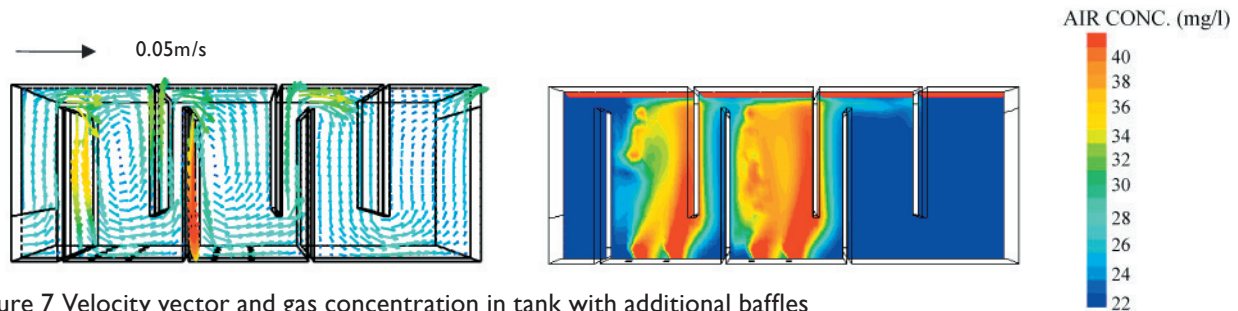


Figure 7 Velocity vector and gas concentration in tank with additional baffles

Continuous Versus Intermittent Ozone Operation

A review of operational procedures at two surface water treatment works was commissioned to assess the impact of continuous versus intermittent ozone operation. The first treatment works, Farmoor AWTW (Figure 9), is the principle treatment works in the Oxford area and involves traditional (chemical) treatment processes. The second site, Kempton Park (Figure 8), incorporates slow sand filter Sandwich™ beds and is one of the large London treatment works.

Past research, site operational software (Surveillance Collection And Data Acquisition: SCADA) and operational and statutory laboratory data were collected from within TWUKI. Where possible, a years worth of data was analysed, with the exception of GAC data, which were projected forward to 2020. From this data cost models were set up and used to assess process costs associated with continuous and intermittent operation of ozone (Table 3).

At Farmoor, no data was available for periods when the ozone was not operational. However, data were available for periods when the pre-ozone only was dosed Table 4.

DISCUSSION & CONCLUSIONS

Copious work has been carried out by Thames Water over the past decade in order to determine and optimise organic, in particular pesticide, removal. Research

commenced in the late 1980's on a 5MLD pilot plant and yielded average reductions in isoproturon and diuron levels of 85% and 74% respectively, at an ozone dose of 2.5 mg/l. This removal rate was generally lower than past research would suggest, although the data seemed more comparable with full-scale operations. The main reason suggested was the influence of background organic levels on ozone use, since the pilot plant treated the same source water as the full-scale plant.

The research was used to determine the optimum operational process, both on plant configuration and operation. CFD modelling was successfully applied to optimise ozone transfer into the water stream in ozone contactors. This paper has discussed work carried out on two designs of multi-compartment ozone contactors. The addition of extra baffles resulted in improved mixing, even though the overall residence time distribution curves were similar.

The assessment of continuous versus intermittent ozone operation highlighted the impact that different treatment processes have on operational costs. Kempton Park, a typical TWUKI SSF works, indicated that considerable operational cost savings, of approximately £200,000 per year, could be made with continuous ozone operation. Although sufficient data was not available to assess the cost benefits at Farmoor (a chemical treatment works), other factors require consideration. Farmoor frequently experiences algal blooms and during such periods ozone enhances the coagulation process, reducing coagulant costs and allowing greater water supply to be achieved.

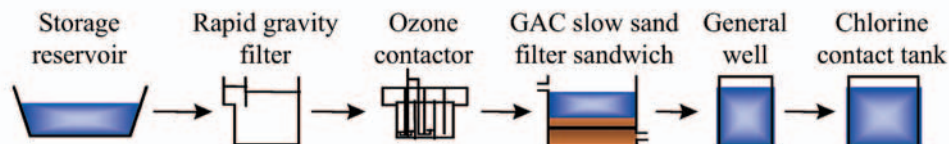


Figure 9 Schematic of Kempton Park

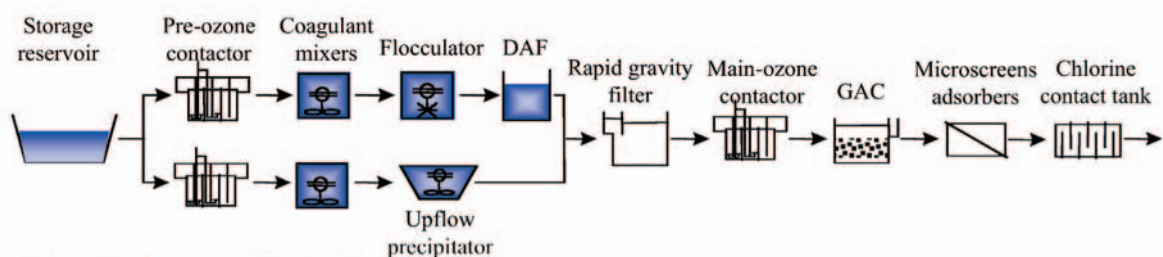


Figure 9 Schematic of Farmoor

Table 3 Approximate cost predictions for Kempton Park for continuous and intermittent ozone operation

Kempton Park - £/yr	With ozone	Without ozone
ozone costs =	123,000	91,000
SSF management costs =	18,000	31,000
GAC management costs =	178,000	411,000
Overall saving per year if ozone run continuously =		£214,000

Table 4 Approximate costs for Farmoor for continuous periods of pre-ozone operational and intermittent periods of main-ozone operation

	Average Pre-Ozone (hours/day)	Average Main-Ozone (hours/day)	Average Ozone Cost (£/day)	Average Chemical Costs (£/day)	Average Total Costs (£/day)
February	24	24	645	231	876
March	24	17	514	238	752
April	24	0	239	230	469
May	24	0	177	-	-

The additional benefits of enhanced taste and odour must also be considered and the reliability of the operational plant. In an industry as strictly regulated as the water industry, ensuring that a process is always available during challenge periods is imperative.

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REFERENCES

- Bauer M, Buchanan B, Colbourne J, Foster D, Goodman N, Kay A, Rachwal A & Sanders T (1994) The GAC Sandwich - from concept to commissioning. *IWSA Specialised Conference on Activated Carbon in Drinking Water Treatment*. 27-28 September, Amsterdam, *Water Supply*, 14: 159 – 175.
- Bourgine F, Chapman J, Bastiment R, Gennery M & Green J (1997) Optimisation of Particle removal in Drinking Water Treatment by the use of Ozone. Presented at *Ozone Workshop*, Warwickshire, Scientific Group of CIWEM.
- Evans H, Bauer B, Luckman I & Page M (2001) An Assessment of the Benefits Afforded by the Continuous Versus Intermittent Operation of Ozone for Drinking Water Treatment. Presented at *The IOA, 15th World Congress*, 10-15 September, Imperial College, London, UK.
- Foster DM, Rachwal AJ & White SL (1991a) Advanced Treatment for the removal of Atrazine and other Pesticides. *IWSA European Specialised Conference: Atrazine And Other Pesticides*, Florence, 23-24 Oct. *Water Supply*, 10.
- Foster DM, Rachwal AJ & White SL (1991b) New Treatment Processes for Pesticide and Chlorinated Organics Control. *J Institute of Water and Environ. Management*, 5(4):466-477.
- Gervai R, Langlais B & Domez F (1989) State of the Art in the designing of Ozone Contact Columns. *Proceeding of the 9th Ozone World Congress*, New York, *Ozone in Wastewater Treatment & Industrial Application*, L. Joseph Bollley (Editor), 2:p486-495.
- Glendinning DJ & Mitchell J (1996) Upgrading water-treatment works supplying Thames Water Ring Main. *J.CIWEM*, 10, February.
- Luckman I (2000) *Assessing the benefits of Ozone use in Chemical Water Treatment*, MSc Thesis, Imperial College of Science, Technology and Medicine, University of London.
- Meijers R, van der Veer A & Kruithof J (1993b) Degradation of pesticides by ozonation and advanced ozonation. *Water Supply*, 11(3/4): pp 309-320.
- Page M (2000) *Assessing the benefits of Ozone in Biological Water Treatment*. MSc Thesis, Imperial College of Science, Technology and Medicine, University of London.
- Rachwal AJ, Foster DM, Holmes M & Hillyer MS (1993) Ozone and Advanced Oxidation Processes for Control of Pesticides and Disinfection By-Products in London's Water Supply. *Proceedings 11th International Ozone Association World Congress*, (2) San Francisco.
- Rachwal AJ, Foster DM & Holmes M (1992) Combining Ozone/Advanced Oxidation and Biological Filtration for Organics Removal from Water. *Proceedings Annual AWWA-WQTC Conference*, Toronto.

- Rachwal AJ, Bauer MJ & West JT (1998) Advanced Techniques for Upgrading Slow Sand Filters. *Slow Sand Filtration - Recent Developments in Water Treatment Technology*, Graham N.J.D. (Editor). Ellis Horwood, Chichester, 349-366.
- Shurrock J, Bauer M, Holmes M & Rachwal A (1998) The use of Advanced Water Treatment Processes for the Reduction of Background Organics and Disinfection By-Products. The Royal Society Of Chemistry International Conference on Disinfection By-Products - The Way Forward. Robinson College, Cambridge 29 March - 1 April.
- Toms, IP Developments in London's water supply system. *Arch. Hydrbiol. Beih. Ergebn. Limnol.*, 28, 149-167 (1987).
- Ta, CT and Hague, J "A Two phase CFD Model for Ozone Tank Design and Trouble Shooting in Water Treatment" Proceedings of 15th World Congress, London, International Ozone Association, Vol III, 188-199 (2001).

THE EFFECT OF NOM CHARACTER ON THE OZONATION OF MIB AND GEOSMIN

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INTRODUCTION

Producing safe drinking water is the major goal for all water authorities. However, consumers judge water by what they see, smell and/or taste. Although poor aesthetic quality does not necessarily imply that the water is unsafe for consumption, it is the basis of many consumer complaints. Of the major aesthetic parameters, tastes and odours (T&O) account for the largest number of consumer complaints in the United States, Japan, Europe and Australia [1,2,3,4].

T&O in drinking water are often due to the presence of trace organic compounds. Two of the most problematic of these compounds are the tertiary alcohols MIB (2-methylisoborneol) and geosmin (*trans*-1,10-dimethyl-*trans*-9-decalol) (Figure 1). These compounds are produced as secondary metabolites by species of cyanobacteria (blue-green algae) and actinomycetes. They impart an earthy/musty odour that can be detected by humans at low concentrations, typically, in the low nanogram per litre level.

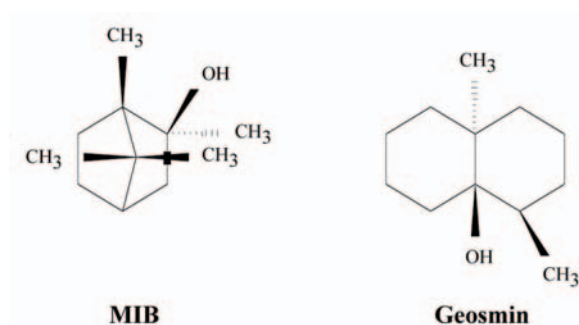
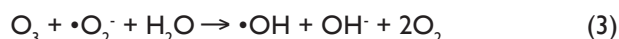
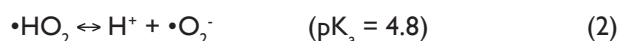


Figure 1. Structures of MIB and geosmin.

MIB and geosmin are not readily removed by conventional water treatment, thus advanced water treatment processes are required. Oxidation by ozone has been shown in some studies to be very effective in removing these compounds [5,6,7]. Ozone is a powerful oxidising agent that is able to react in natural waters via two competing pathways: direct oxidation by the O₃ molecule and indirect oxidation by the hydroxyl (OH) radical. Direct oxidation occurs through highly selective and relatively slow reactions whereas indirect oxidation

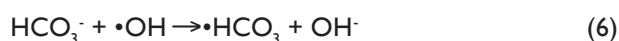
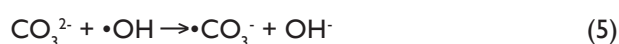
reactions tend to be very fast and nonselective [8]. The OH radical generated via indirect oxidation is a more powerful oxidant than the O₃ molecule and has been found to readily destroy aliphatic compounds such as MIB and geosmin [9,10].

There are many substances in natural waters that are able to initiate the formation of OH radicals, including dissolved aqueous iron (III), hydrogen peroxide and natural organic material (NOM) [9]. In addition, UV radiation has also been known to propagate the formation of the OH radical [11,12]. In pure water, molecular ozone is known to self-decompose by the reaction with hydroxide ions. The following is a proposed reaction scheme based on models developed by Staehelin and Hoigne [13] and Yurteri and Gurol [14]:



On the basis of the above scheme, the reaction of molecular ozone and hydroxide ion yields two moles of superoxide radicals ($\cdot\text{O}_2^-$) (reactions 1 and 2) when the pH is above 4.8. Molecular ozone is then decomposed by the attack of the superoxide radical which results in the production of the hydroxyl radical ($\cdot\text{OH}$) (reaction 3). The decomposition cycle can continue by the reaction of molecular ozone with the hydroxyl radical (reaction 4). Therefore, it is clear that pH plays an important role in the ozonation process. The higher the concentration of hydroxide ions, the higher the concentration of OH radicals.

Alkalinity can also affect the ozonation process. Although carbonate and bicarbonate ions do not react with molecular ozone, they are known scavengers of OH radicals [15]:



Therefore, due to reactions 5 and 6, molecular ozone remains relatively stable, which results in low concentrations of OH radicals. As MIB and geosmin are considered to be susceptible to attack by OH radicals, this would ultimately lead to a reduction in the efficiency of the oxidation of both compounds.

There have been many studies of the ozonation of MIB and geosmin with conflicting results. Studies conducted by Lalezary *et al.* [16] indicated that low doses of ozone (2 mg/L) achieved low removals of geosmin (20 %) in spiked, organic free water. Other researchers have found that doses between 2 and 7 mg/L of ozone were sufficient to destroy MIB and geosmin in natural waters [5,6]. These results led to the conclusion that the presence of NOM enhanced the destruction of the compounds [9]. Natural waters contain NOM capable of initiating the formation of the OH radical, leading to higher levels of the radical, and consequently higher removals of the T&O compounds.

Morioka *et al.* [17] studied the kinetics of MIB and geosmin decomposition by ozonation in the presence of dissolved inorganic and organic substances in raw water. Sodium carbonate and sodium hypochlorite were used as representatives of the inorganic substances whereas alcohols, volatile fatty acids and humic substances (humic and fulvic acids) were chosen as representatives of the organic substances in raw water. They determined that the decomposition of MIB and geosmin followed first-order reactions and that the first-order constants decreased with increasing concentrations of carbonate ion, free chlorine, alcohols and volatile fatty acids. In contrast, the humic substances (at DOC concentrations of 3 mg/L) were found to enhance the rate of decomposition with humic acids promoting a higher decomposition of MIB than fulvic acids. Their study demonstrated that the oxidation of MIB and geosmin was predominantly through the OH radical and that the presence of humic substances enhanced the decomposition of MIB and geosmin.

It is clear that water quality factors such as the NOM concentration, alkalinity and pH all have a significant impact on the ozonation of MIB and geosmin. However, to date, no information has been published on the effect the NOM character has on this process. The study by Morioka *et al.* [17] suggested that the characteristics of humic substances may play an important role in the formation of OH radicals, however, the authors were unable to elaborate on this. The aim of this study was to determine the influence of NOM character on the ozonation of MIB and geosmin. In addition, the effect of a radical scavenger on the ozonation of MIB and geosmin (in the presence of different NOM fractions) will also be studied to confirm the theory that the oxidation of MIB and geosmin is primarily through the OH radical.

MATERIALS AND EXPERIMENTAL METHODS

Materials and Reagents

All reagents used were analytical grade. Solutions were made using Milli-Q water (Millipore Pty Ltd). Stock solutions of MIB and geosmin (Ultrafine Chemicals) were prepared by two different methods: by dissolving in acetone and by dissolving in Milli-Q water. Raw water was collected from Myponga Reservoir, South Australia and filtered through a 0.45 µm cartridge filter (US Filter). Synthetic waters were prepared by adding known concentrations of the NOM fractions into Milli-Q water containing 0.01 M NaCl (NaCl was added to maintain the ionic strength of the water). The pH was stabilised in selected experiments with 1 mM phosphate buffer (pH 7). The alkalinity was varied in a controlled fashion in selected experiments with the addition of sodium bicarbonate at pH 7 (50 and 200 mg/L as CaCO₃).

Three resins were used for the isolation of NOM from Myponga Reservoir: XAD 4 resin (Supelco), DAX 8 resin (Supelco) and MIEX[®] DOC resin¹ (Orica Pty Ltd). Ultrafiltration membranes were Amicom Ym03 and Yc05 (Adelab Scientific). The nominal molecular weight (MW) cut-offs of the membranes were 3000 and 500 Dalton respectively. Resins and membranes were pretreated according to methods outlined in Hepplewhite [18].

EXPERIMENTAL METHODS

Isolation and Fractionation of NOM

NOM, isolated using MIEX[®] anion exchange, was fractionated into nominal MW fractions <500, 500-3000 and >3000 according to methods described in Hepplewhite [18]. The effluent from the MIEX[®] column was concentrated using reverse osmosis, adjusted to pH 2 and passed through a XAD 4/DAX 8 mixed resin bed. The adsorbed NOM was eluted from the mixed resin using NaOH and acetonitrile according to methods described in Aiken *et al.* [19] and Aiken and Leenheer [20]. The procedure resulted in five Myponga NOM fractions which are described in Table 1.

Table 1. Descriptions of Myponga NOM fractions and their abbreviations.

Myponga NOM fraction descriptions	Abbreviation
MIEX [®] isolate <500	F1
MIEX [®] isolate 500-3000	F2
MIEX [®] isolate >3000	F3
MIEX [®] effluent concentrated using XAD 4/DAX 8 eluted with NaOH	EN
MIEX [®] effluent concentrated using XAD 4/DAX 8 eluted with acetonitrile	EA

Laboratory Scale Ozonation Experiments

Batch scale ozonation experiments were conducted using an Ozonia CFS-IA ozone generator fed with HPLC grade oxygen (Air Liquide). In this process ozone gas was bubbled through a 1 L batch reactor containing ozone demand-free water at 4°C. Typical ozone stock solution concentrations ranged between 35–40 mg/L. Ozone stock solution and residual concentrations were measured using the Indigo Colorimetric Method [21]. All ozonation experiments were conducted at 20°C and pH 7.

The natural and synthetic waters were spiked with 100 ng/L of both MIB and geosmin and ozonated by adding aliquots of the ozone stock solution to obtain the desired ozone doses. All experiments were performed in duplicate. One duplicate sample was quenched for 5 minutes with HPLC grade nitrogen gas (Air Liquide) after a 5 minute ozone contact time, whilst the other was quenched with Indigo Reagent 2 after a 5 minute ozone contact time for the measurement of the ozone residual [21]. The sample quenched with nitrogen gas was retained for the following analyses: MIB and geosmin analyses, UV absorbance, colour, DOC, pH and high performance size exclusion chromatography (HPSEC).

Ozone decomposition experiments were conducted on the synthetic waters at an ozone dose (mg/L) / DOC (mg/L) ratio of 1:1. In these experiments, the synthetic waters were prepared in a 500 mL batch reactor by spiking the appropriate concentrations of the NOM fractions into Milli-Q water containing 0.01 M NaCl and 1 mM phosphate buffer (pH 7). Ozone was injected into the batch reactor which was then agitated to ensure sufficient ozone transfer in the liquid phase. Aliquot samples were taken at various time intervals and added to Indigo Reagent 2 to determine ozone concentrations over the specific time intervals.

Analytical Methods

Measurements of UV absorbance and colour were carried out on a GBC UV/VIS 918 Spectrophotometer.

UV absorbance was measured at 254 nm in a 1 cm quartz cell. Colour was measured by comparing the absorbance of the sample at 456 nm (in a 5 cm quartz cell) with a platinum/cobalt standard (50 Hazen Units (HU)). Specific UV absorbance (SUVA) and specific colour were calculated as follows:

$$\text{SUVA} = \text{UV absorbance @ 254 nm} / \text{DOC (mg/L)} \times 100$$

$$\text{Specific Colour} = \text{Colour (HU)} / \text{DOC (mg/L)}$$

Ozone residuals (via Indigo Reagent 2 at a wavelength of 600 nm) were measured on a portable Shimadzu UVmini 1240 Spectrophotometer using a 5 cm quartz cell. DOC was measured using a Sievers 820 Total Organic Carbon Analyser. Measurements of pH were conducted on a Beckman PHI 50 pH Meter. HPSEC analyses were conducted based on the method by Chin *et al.* [22]. ¹³C-NMR results were obtained using methods described in Hepplewhite [18]. MIB and geosmin analyses were conducted using solid phase microextraction (SPME) and gas chromatography-mass spectrometry (GC-MS).

RESULTS AND DISCUSSION

Preliminary Ozonation Experiments

The effect of solvent

Nearly all studies using MIB and geosmin involve preparing stock solutions of both compounds by dissolving in an organic solvent such as methanol or acetone as both compounds are difficult to dissolve directly in water. However, the solubility of each compound indicates that they are reasonably soluble in water (MIB-194.5 mg/L, Geosmin-150.2 mg/L) [23]. There was a concern that the presence of an organic solvent may affect the ozonation process. Thus, a preliminary experiment was performed to determine if there was a difference in the ozonation of MIB dissolved in acetone or Milli-Q water. Figure 2 represents the destruction of MIB spiked from the different stock solutions into two waters: Milli-Q water (NOM-free) and Myponga raw water (DOC-11.0 mg/L). There is clearly an effect of the presence of acetone, which results in a decreased destruction of MIB in the samples spiked with acetone stock (Figure 2A). Spiking

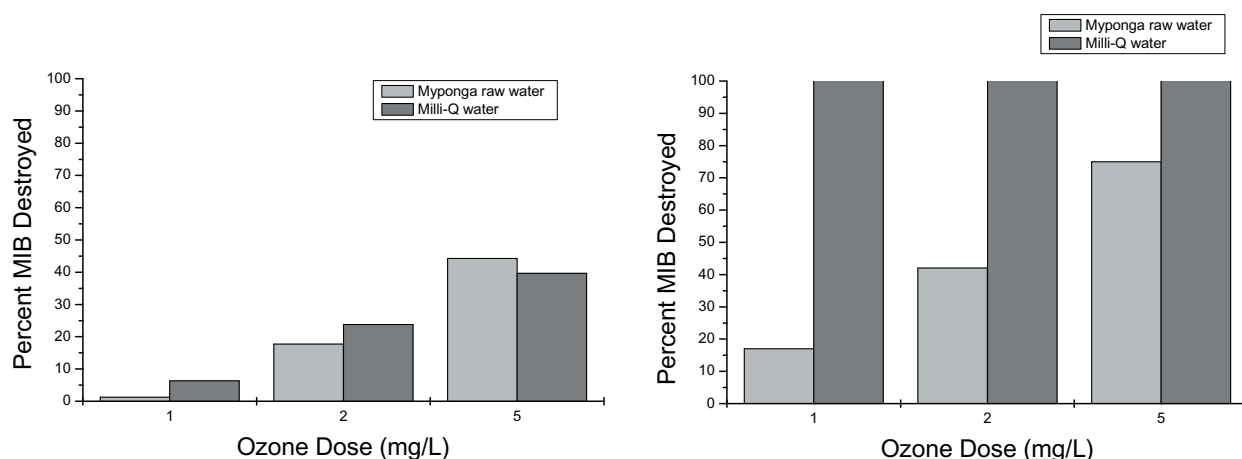


Figure 2. Destruction of MIB dissolved in: (A) Acetone. (B) Milli-Q water.

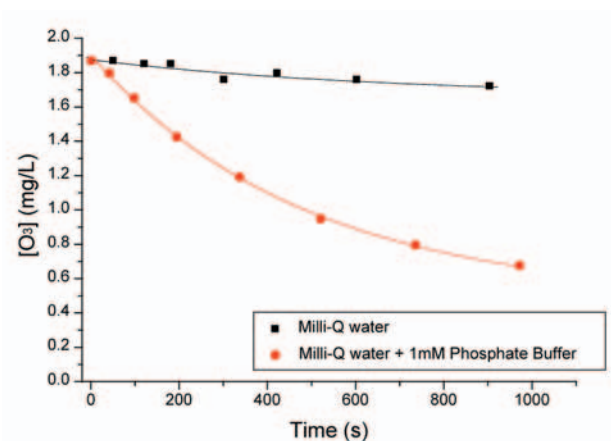


Figure 3. The effect of 1 mM phosphate buffer in the decomposition of ozone in Milli-Q water.

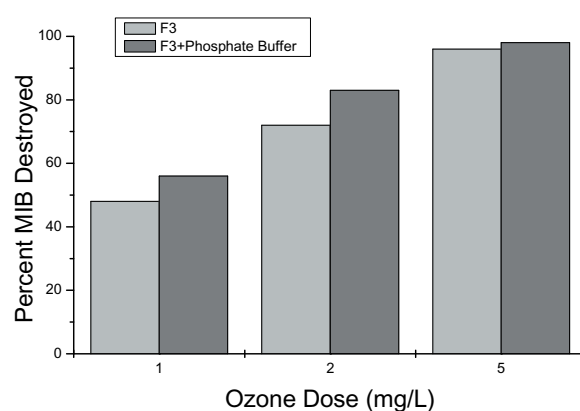


Figure 4. The effect of 1 mM phosphate buffer on the ozonation of Myponga NOM fraction F3.

the water with the acetone stock solution resulted in a 10 mg/L increase in DOC concentration. Acetone has been documented to react with OH radicals through hydrogen abstraction reactions with rate constants approximately 4.5 times faster than that of bicarbonate ions [15]. Therefore, we can assume that acetone has acted as an OH radical scavenger. Consequently, all subsequent ozonation experiments were conducted with MIB and geosmin dissolved in Milli-Q water.

The effect of phosphate buffer

Previous studies have indicated that pH has an effect on the ozonation of MIB and geosmin [10]. At higher pH values, higher concentrations of hydroxide ions are present, which lead to the decomposition of ozone, initiating higher concentrations of OH radicals. Because of this, a suitable pH buffer was required in this study to stabilise pH.

The most commonly used pH buffers in ozonation experiments are phosphate buffers. However, phosphate ions have been reported to act as promoters of the decomposition of molecular ozone [24]. An ozone decomposition experiment was conducted at pH 7 with Milli-Q water and Milli-Q water containing 1 mM of phosphate buffer (Figure 3). The result indicates that the presence of phosphate buffer significantly increases the decomposition of ozone.

Figure 4 illustrates the effect phosphate buffer has on the ozonation of MIB in a synthetic water containing F3. As one can see, the addition of phosphate buffer increases the destruction of MIB at all ozone doses (1, 2 and 5 mg/L) after a 5 minute contact time. The same trends were also observed with the ozonation of geosmin.

Several alternatives to the phosphate buffer were also investigated. However, all were found to affect the ozonation process in some way. Two effects were encountered in these preliminary experiments:

Phosphate buffers act as promoters of the decomposition of molecular ozone; and Variations in pH affect ozonation reactions, with high pH values also promoting the decomposition of molecular ozone.

Further experiments were conducted in the presence and absence of phosphate buffers with the knowledge of these effects.

THE EFFECT OF NOM CHARACTER ON THE OZONATION OF MIB AND GEOSMIN

Characterisation of Myponga NOM Fractions

Table 2 lists the total DOC in each of the Myponga NOM fractions and the percent of the total DOC each fraction represents. Approximately 36% of the total DOC from Myponga raw water was not recovered during the isolation and fractionation procedures. This is due to the small losses of DOC in each of the isolation and fractionation steps.

Table 2. The total DOC present in the Myponga NOM fractions and the percent of the total DOC passed through the isolation and fractionation procedures.

Sample	Total DOC in Fraction (mg)	Percent of Total DOC from Raw Water
F1	170	6 %
F2	900	32 %
F3	250	10 %
EN	100	4 %
EA	365	12 %

The Myponga NOM fractions were characterised using HPSEC, UV/visible absorbance and ^{13}C -NMR. All the NOM fractions exhibited different molecular weight distributions as shown in Figure 5. The MIEX[®] NOM fractions (F1, F2 and F3) all contained compounds in the higher molecular weight range (above 2000 Daltons) whereas the effluent NOM fractions, EA and EN, contained no UV/visible absorbing compounds greater than 2000 Daltons. This is evident with the low weight- (M_w) and number-averaged (M_n) average molecular weight values for EA and EN in Table 3. The apparent molecular weight at the highest point in each chromatogram (M_p) is also listed in Table 3.

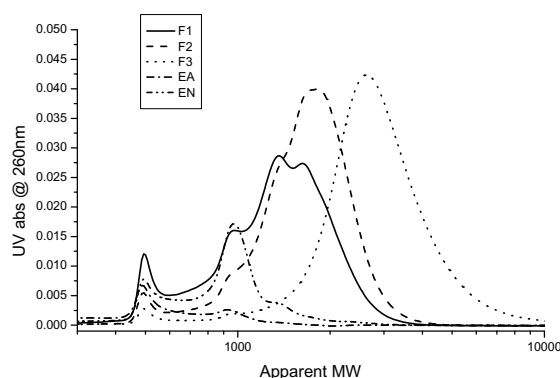


Figure 5. HPSEC chromatograms of Myponga NOM fractions.

Table 3. The M_w , M_n and M_p of the Myponga NOM fractions.

Sample	M_w	M_n	M_p
F1	1010	745	980
F2	1680	1430	1820
F3	2960	2340	2630
EN	630	400	650
EA	260	180	250

The UV/visible absorbance of each of the NOM fractions is also different as shown with the SUVA and specific colour values listed in Table 4. In general, the MIEX[®] concentrated NOM fractions contained a higher concentration of UV/visible absorbing compounds.

Table 4. SUVA and specific colour of Myponga NOM fractions.

Sample	SUVA (L/mg-cm)	Specific Colour (HU-L/mg)
F1	3.9	3.0
F2	4.3	4.6
F3	5.4	15.4
EN	1.6	0.8
EA	1.6	0.6

Figure 6 illustrates the ^{13}C -NMR spectra of the NOM fractions. Unfortunately the authors were unable to obtain separate spectra for both F2 and F3 due to time restraints, however, a combined spectra of F2/F3 is presented. The MIEX[®] NOM fractions (F1, F2/F3) contained more aromatic carbon compounds than the effluent NOM fractions (EA and EN) as evident in the peak at 130 ppm.

There were slight differences between the MIEX[®] NOM fractions in the 0-110 ppm range. The alkyl region (0-50 ppm) was more defined for F1 compared with F2/F3. In addition, the peak area between 29-33 ppm in F1 indicates that it has a high number of methylene carbons in branched alkyl chains. There were also slight differences between the two effluent NOM fractions with EN having a more similar spectra to the MIEX[®] NOM fractions than EA. The major difference between the effluent NOM fractions is the carboxyl carbon region (165-190 ppm) which is more defined for EN than EA.

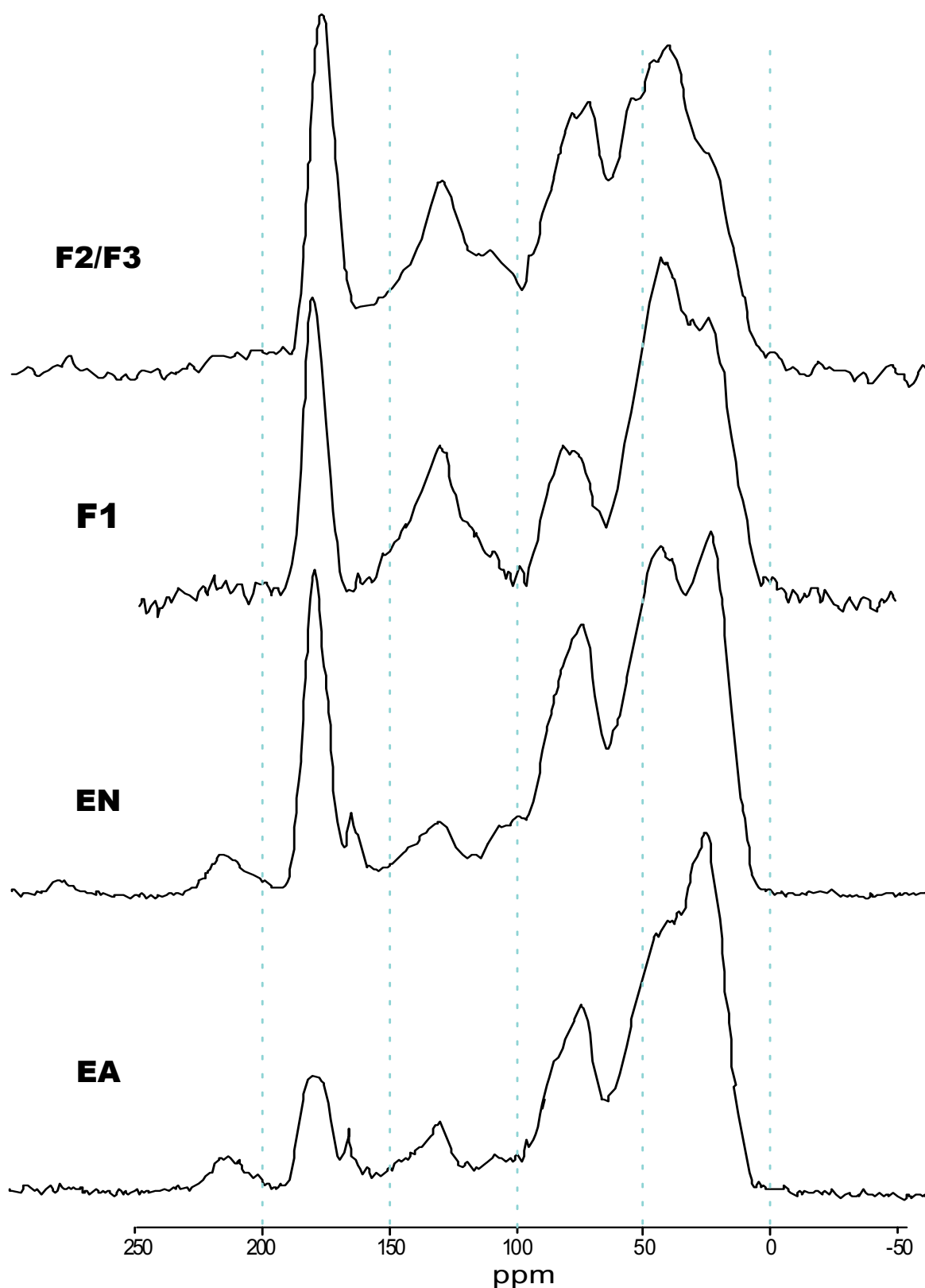


Figure 6. ^{13}C -NMR spectra of the Myponga NOM fractions.

Buffered Ozonation Experiments

Ozone decomposition experiments were conducted on the five synthetic waters at an ozone dose (mg/L)/DOC (mg/L) ratio of 1:1 (Figure 7A). Faster ozone decomposition was observed in the MIEX[®] NOM

fractions compared with the effluent NOM fractions. Most of the molecular ozone was completely decomposed after 5 minutes in the MIEX[®] NOM fractions, with the order of increasing ozone decomposition following the trend, $\text{F3} > \text{F2} > \text{F1}$.

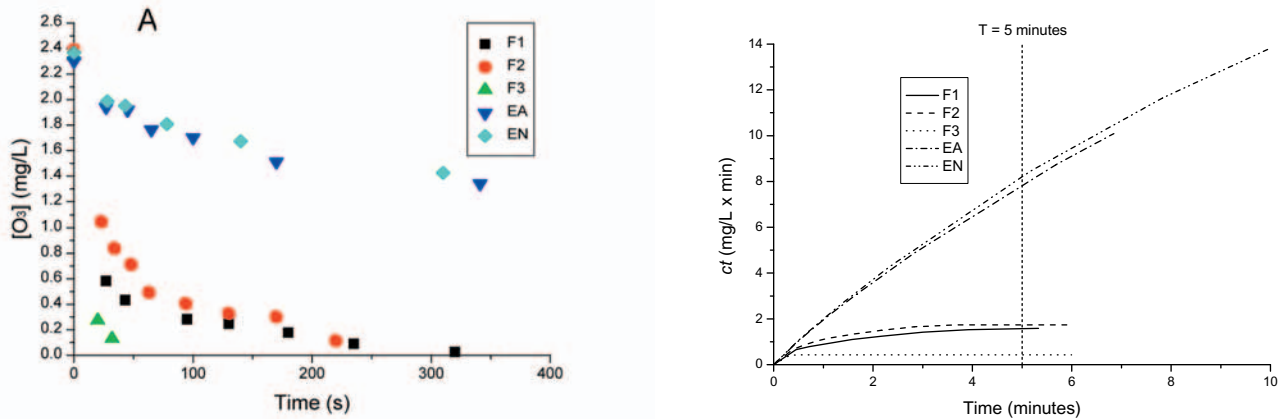


Figure 7. (A) Ozone Decomposition in Myponga NOM fractions. (B) Ozone exposures (*ct*) of Myponga NOM fractions.

The ozone exposures (*ct*) of the NOM fractions were calculated from the integrals of the decomposition curves in Figure 7A and plotted against time (Figure 7B). The ozone exposure (*ct*) is used as a standard measure for the ozone concentration acting during a reaction time. High *ct* values were observed for the effluent NOM fractions at all times compared with the low *ct* values of the MIEX[®] NOM fractions.

The next step involved spiking MIB and geosmin into the five synthetic waters at concentrations of 100 ng/L. However, the initial concentration of the NOM in the synthetic waters was increased to 5 mg/L. The synthetic waters were ozonated at doses of 1, 2 and 5 mg/L for a contact period of 5 minutes.

The MIEX[®] NOM fractions (which contained the more highly coloured, higher molecular weight compounds) consumed all of the ozone after 5 minutes. In contrast, the effluent NOM fractions (containing the lower molecular weight, low colour compounds) exhibited low ozone demands (high ozone residuals) (Table 5). This indicates that the decomposition of ozone during the 5 minute contact time was facilitated by reaction with the UV/visible light chromophores, generally considered more susceptible to oxidation [25].

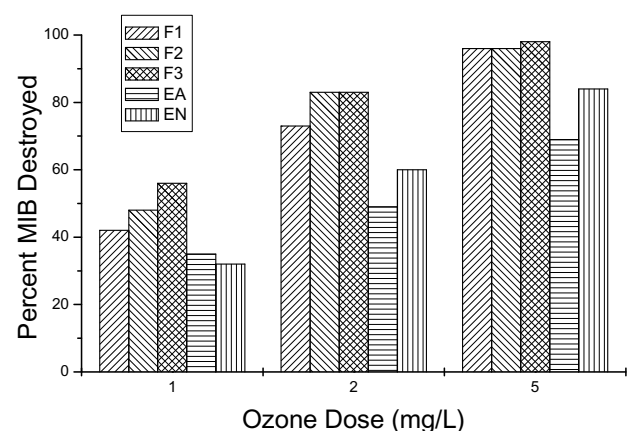
Table 5. Ozone residuals as a function of ozone dose for the effluent NOM fractions.

Ozone dose (mg/L)	Ozone residual (mg/L)	
	EA	EN
1	0	0
2	0.3	0.2
5	1.1	1.0

MIB removal was found to increase with increased ozone dose in all five fractions with up to 98% removal with the highest ozone dose (Figure 8). The removal of geosmin followed the same trend, however, it was found to be slightly easier to remove than MIB. These results are consistent with previous studies [16]. The destruction of

MIB and geosmin was influenced by the character of the NOM fractions. The decrease in both MIB and geosmin concentration was significantly higher in F3 than in EA at all ozone doses. For example, at an ozone dose of 2 mg/L, the removals of MIB were 83% and 49% respectively. The removal of the compounds in the other NOM fractions showed the same trends, increasing MIB and geosmin removal with increasing UV/visible absorbing character of the NOM. Other researchers have suggested that the mechanism of destruction of MIB and geosmin by ozone is via the OH radical, a much stronger and quicker oxidising agent than the O₃ molecule. The formation of the radical is promoted in the reaction of molecular ozone with NOM, therefore it is believed that the samples with the highest ozone demand may also produce the highest concentration of OH radicals for a given reaction time. This, in turn, would lead to higher removals of the taste and odour compounds.

Figure 8. Removal of MIB in the presence of Myponga NOM Fractions in Milli-Q water (buffer present).



The 1:1 ozone dose/DOC (5 mg/L/5 mg/L) results were compared with their corresponding *ct* values at 5 minutes for all the NOM fractions (Table 6). The results suggest that low *ct* values correspond to an increase in the destruction of MIB. Similar observations were made with the ozonation of geosmin.

Table 6. The percent destruction of MIB as a function of ozone exposure (ct) at 5 minutes.

NOM Fraction	Ozone exposure (ct)	Percent MIB destroyed
F1	1.6	96
F2	1.7	96
F3	0.4	98
EN	8.2	84
EA	7.8	69

Unbuffered Ozonation Experiments

Five synthetic waters were prepared and ozonated in the same manner as that of the buffered ozonation experiments without the addition of phosphate buffer. The same trends were seen as with the buffered ozonation experiments, ie. increasing MIB and geosmin removal with increasing ozone dose. Similar trends were also seen with the removal of MIB and geosmin at all ozone doses, although lower removals were seen with these experiments compared with the buffered ozonation experiments. This is presumably due to the pH of the unbuffered samples which was at pH 6 as opposed to the buffered experiments where all samples were at pH 7. The pH of the unbuffered ozonated samples was found to decrease by up to 1 pH unit during ozonation. This is consistent with literature which states that acidity increases after the ozonation of NOM [26]. The substantial decrease in pH indicates that there is a need to stabilise pH with a suitable buffer to negate the effects of pH which have been documented to affect the ozonation process.

HPSEC analyses were conducted on all of the ozonated samples. The results are presented in Figure 9. The UV absorbance of all the NOM fractions decreased with increasing ozone dose. However, interesting chromatograms were observed with F3 and EA. In the F3 chromatogram, there was a gradual shift of the peak to the left with increasing ozone dose. This indicates that the higher molecular weight compounds are being broken down. In the EA chromatogram, the UV absorbances of the ozonated samples, above 1000 Daltons, are higher than the UV absorbance of the unozonated control sample. This could be due to the oxidative polymerisation of smaller molecular weight compounds into larger molecular weight compounds. Alternatively, another explanation for this could be due to the formation of intermediate ozonation by-products, in the same molecular weight region, which contain higher UV absorbing properties. Similar results were obtained in a study by Bose *et al* [26] where slight increases in apparent molecular size were evident after low doses of ozone were applied to low molecular weight NOM fractions (<500 Daltons).

The Effect of a Radical Scavenger on the Ozonation of MIB and Geosmin

Synthetic waters were prepared by adding 2.5 mg/L of the NOM fractions into Milli-Q water containing 0.01 M NaCl. The pH was stabilised by the addition of 1 mM phosphate buffer (pH 7). Sodium bicarbonate was added to the synthetic waters as a radical scavenger at concentrations of 50 and 200 mg/L as CaCO_3 . Ozone doses of 0.5, 1.0 and 2.5 mg/L were applied to the synthetic waters. The ozone doses applied corresponded to the same ozone dose (mg/L)/DOC (mg/L) ratio as the buffered ozonation experiments. Results for the ozonation of MIB in the synthetic waters for F1 and F3 are presented in Figure 10.

The oxidation of MIB decreased with increasing concentration of bicarbonate. The same trends were observed with geosmin. This is consistent with previous studies [17]. These results support the theory that the oxidation of MIB and geosmin is primarily via the OH radical since bicarbonate ions act to scavenge the OH radical which stabilises molecular ozone, resulting in a decrease in the oxidation of the MIB and geosmin.

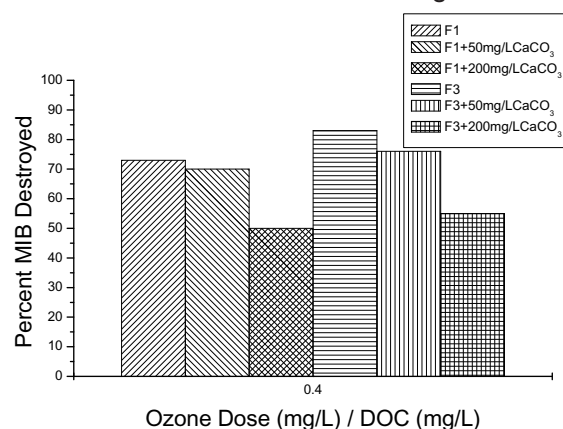


Figure 10. The destruction of MIB in the presence of Myponga NOM fractions F1 and F3 with: no radical scavenger, radical scavenger at 50 mg/L as CaCO_3 and radical scavenger at 200 mg/L as CaCO_3 .

SUMMARY AND CONCLUSIONS

Results from the preliminary ozonation experiments indicate that MIB and geosmin can be dissolved in Milli-Q water. In addition, the matrix which is used to dissolve these compounds is very important in terms of the ozonation of both MIB and geosmin. Solvents such as methanol have previously been reported to affect the ozonation process by decreasing the decomposition of molecular ozone, and hence decreasing the removal of MIB and geosmin [17]. Similar findings were observed in this study when dissolving MIB and geosmin in acetone.

The addition of a phosphate buffer was found to affect the ozonation of MIB and geosmin by promoting the decomposition of molecular ozone. This, in turn, lead to an increase in the destruction of both MIB and geosmin.

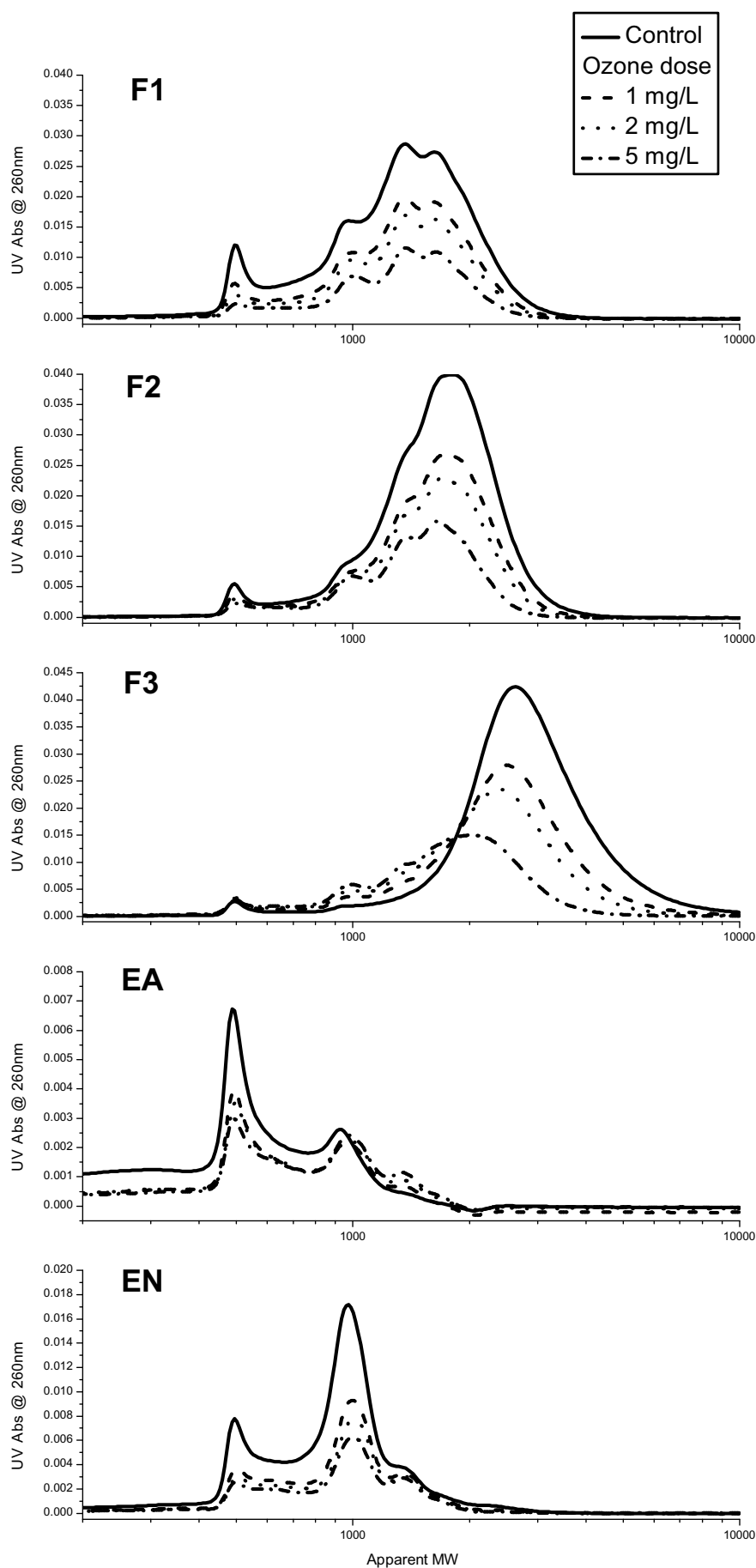


Figure 10. HPSEC chromatograms of ozonated Myponga NOM fractions.

The NOM character had a significant impact on the decomposition of ozone. Low *ct* values were observed for the MIEX® NOM fractions as opposed to the high *ct* values obtained for the effluent NOM fractions. The NOM character also had a significant effect on the ozonation of MIB and geosmin. Higher MIB and geosmin removals were observed in the MIEX® NOM fractions compared with the effluent NOM fractions. In general, the destruction of MIB and geosmin was facilitated by NOM which contain high molecular weight, high UV/visible absorbing components. This observation is consistent with the theory of OH radical formation, i.e. the formation of the OH radical is promoted in the reaction of molecular ozone with NOM. The results suggest that low *ct* values correspond to an increased destruction of MIB and geosmin. Therefore the presence of an ozone residual may not necessarily be beneficial in water treatment, especially when T&O compounds are concerned.

The presence of bicarbonate, a radical scavenger, was found to decrease the efficiency of the ozonation of MIB and geosmin in all the NOM fractions. As the concentration of bicarbonate was increased, the destruction of MIB and geosmin decreased. This supports the theory that the oxidation of MIB and geosmin is primarily through the OH radical.

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REFERENCES

- 1) Herzing DR, Snoeyink VL and Wood NF (1977) Activated Carbon Adsorption of the Odorous Compounds 2-Methylisoborneol and Geosmin. *Journal AWWA*, **69**, pp. 223-228.
- 2) Suffet IH, Corado A, Chou D, Butterworth S and McGuire MJ (1994) AWWA Taste and Odor Survey. *Proceedings – AWWA Water Quality Technology Conference*, pp. 1785-1831.
- 3) Hayes KP, Graham DK, Simpson KL and Stockham PC (1996) Off-flavours in drinking water – experiences of a South Australian water authority. *Technical proceedings of 10th IWSA – ASPAC regional conference and exhibition, Hong Kong*, pp. 189-197.
- 4) Kageyama K, Watanabe S, Baba K, Komatsu N and Yamakoshi N (1996) Overall Chemical Reaction Model of an Ozone Contactor for a Water Purification Model. *Water Science & Technology*, **34** (3/4), pp.195-202.
- 5) Lundgren BV, Grimvall A and Savenhed R (1988) Formation and Removal of Off-flavour Compounds During Ozonation and Filtration Through Biologically Active Sand Filters. *Water Science & Technology*, **20** (8/9), pp. 245-253.
- 6) Terashima K (1988) Reduction of Musty Odor Substances in Drinking Water - A Pilot Plant Study. *Water Science & Technology*, **20** (8/9), pp. 275-281.
- 7) Ferguson DW, McGuire MJ, Koch B, Wolfe RL and Aieta EM (1990) Comparing PEROXONE and Ozone for Controlling Taste and Odor Compounds, Disinfection By-products, and Microorganisms. *Journal AWWA*, **82** (4), pp. 181-191.
- 8) Singer PC (1990) Assessing Ozonation Research Needs in Water Treatment. *Journal AWWA*, **82** (10), pp. 78-86.
- 9) Glaze WH, Schep R, Chauncey W, Ruth EC, Zarnoch JJ, Aieta EM, Tate CH, and McGuire MJ (1990) Evaluating Oxidants for the Removal of Model Taste and Odor Compounds from a Municipal Water Supply. *Journal AWWA*, **82** (5), pp. 79-84.
- 10) Motoyama N, Morioka T, Shimizu Y, Hoshikawa H, Okada M and Moniwa T. (1990) The Effect of Organic Substances on the Ozonation of Musty Odor Substances in Water. *Water Supply*, **8** (3/4), pp. 475-482.
- 11) Benitez FJ, Beltrán-Heredua J and Gonzalez T (1994) Degradation by Ozone and UV Radiation of the Herbicide Cyanazine. *Ozone: Science & Engineering*, **16**, pp. 213-234.
- 12) Beltrán FJ (1999) Estimation of the Relative Importance of Free Radical Oxidation and Direct Oxidation/UV Radiation Rates of Micropollutants in Water. *Ozone: Science & Engineering*, **21**, pp. 207-228.
- 13) Staehelin J and Hoigne J (1982) Decomposition of Ozone in Water: Rate of Initiation by Hydroxide Ions and Hydrogen Peroxide. *Environmental Science & Technology*, **16** (10), pp. 676-681.
- 14) Yurteri C and Gurol MD (1988) Ozone Consumption in Natural Waters: Effects of Background Organic Matter, pH and Carbonate Species. *Ozone: Science & Engineering*, **10**, pp. 277-290.
- 15) Hoigne J and Bader H (1976) The Role of Hydroxyl Radical Reactions in Ozonation Processes in Aqueous Solutions. *Water Research*, **10**, pp.377-386.
- 16) Lalezary S, Pirbazari M and McGuire MJ (1986) Oxidation of Five Earthy-Musty Taste and Odor Compounds. *Journal AWWA*, **78** (3), pp. 62-69.
- 17) Morioka T, Motoyama N, Hoshikawa H, Murakami A, Okada M and Moniwa T (1993) Kinetic Analysis on the Effect of Dissolved Inorganic and Organic Substances in Raw Water on the Ozonation of Geosmin and 2-MIB. *Ozone: Science & Engineering*, **15** (1) pp. 1-18.

- 18) Hepplewhite C (2000) The Isolation, Fractionation and Characterisation of NOM from Water and Its Effect on the Adsorption of Taste and Odour Compounds by Activated Carbon. *PhD Dissertation*, University of South Australia.
- 19) Aiken GR, Thurman EM and Malcolm RL (1979) Comparison of XAD Macroporous Resins for the Concentration of Fulvic Acid from Aqueous Solution. *Analytical Chemistry*, **51** (11), pp. 1799-1803.
- 20) Aiken GR and Leenheer JA (1993) Isolation and Chemical Characterisation of Dissolved and Colloidal Organic Matter. *Chem. and Ecol.*, **8** (3), pp. 135-151.
- 21) APHA, AWWA, WEF. (1998) *Standard Methods for the Examination of Water and Wastewater*, 20th Edition. Washington, DC, American Public Health Association.
- 22) Chin YP, Aiken G and O'Loughlin E (1994) Molecular Weight, Polydispersity, and Spectroscopic Properties of Aquatic Humic Substances. *Environmental Science & Technology*, **28** (11), pp. 1853-1858.
- 23) Pirbazari M, Borow HS, Craig S, Ravindran V and McGuire MJ (1992) Physical Chemical Characterization of Five Earthy-Musty-Smelling Compounds. *Water Science & Technology*, **2**, pp. 81-88.
- 24) Staehelin J and Hoigne J (1985) Decomposition of Ozone in Water in the Presence of Organic Solutes Acting as Promoters and Inhibitors of Radical Chain Reactions. *Environmental Science & Technology*, **19** (12), pp. 1206-1213.
- 25) Croué J-P (1999) Isolation, Fractionation, Characterization and Reactive Properties of Natural Organic Matter. *Proceedings – 18th Federal AWWA Convention, Adelaide, Australia*.
- 26) Bose P, Bezbarua BK and Reckhow DA (1994) Effect of Ozonation on Some Physical and Chemical Properties of Aquatic Natural Organic Matter. *Ozone: Science & Engineering*, **16**, pp. 89-112.

HIGH QUALITY DRINKING WATER THROUGH ADVANCED TREATMENT PROCESS FOR NOOSA COUNCIL

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EXECUTIVE SUMMARY

Noosa Council undertook an upgrade of their water treatment plant to meet increasing demand and improve water quality through a design build operate (DBO) project. The Noosa area is a major tourist destination on the Sunshine Coast in Queensland and supplying high quality safe water is important to the region. Vivendi Water Australia (VWA) was the successful tenderer for the DBO project and supplied world's best practice technology to achieve the water treatment upgrade.

Manganese had been a concern for Noosa Council with regular fluctuations in manganese levels up to 0.40 mg/L in the raw water. Taste and odour problems had been experienced in Noosa and removal of these compounds was considered important. Other water quality issues considered possible scenarios at Noosa were *Cryptosporidium* and *Giardia* parasites and cyanobacterial toxins.

Noosa Council developed water quality performance levels to ensure the supply of high quality water and address the particular water quality issues of concern, with the Noosa water supply. This included meeting the latest NHMRC guidelines as well as higher water quality standards on a number of parameters. The standards applied are: manganese <0.01 mg/L, turbidity <0.3 NTU, colour <5HU, particle counts <100 counts/ml or >3 log removal, THMs <50 µg/L and removal of algal toxins and taste and odour. The Flavour Profile Analysis (FPA) technique was used for taste and odour assessment and the mouse bioassay for algal toxins. The plant is to be upgraded in stages from its present capacity of 37 MLD to 56 MLD.

To achieve these standards and achieve increased capacity, VWA applied a multistaged continuous process. This process includes: potassium permanganate dosing together with pre-filter chlorination and coated media filtration to remove manganese; improvements to the coagulation process; installation of dual media filter beds, using sand and Australia filter coal in the existing filters; polymer addition before the clarifiers and filters to achieve improved turbidity, colour and particle removal; and the ozone and biological activated carbon (BAC) process to reduce THM levels, remove algal toxins and taste and odours. The processes were extensively tested in pilot plant studies to develop design criteria and confirm their capability to achieve the water quality targets. These processes and results of testing are presented and discussed.

The potassium permanganate dosing with pre-filter chlorination achieved filtered water manganese levels of <0.01 mg/L with raw water manganese levels of >0.3 mg/L. The ozone BAC process achieved a 20-30% removal in DOC (from an average 3.5 mg/L to 2.4 mg/L) allowing a reduction in chlorine demand and THM levels in the final water of <50 µg/L. Bromate levels of <20 µg/L were maintained in the final water. Taste and odour compounds MIB and geosmin were effectively removed in the ozone BAC step with partial removal in the ozone step. Particle removal was maintained at <100 counts per ml by employing polymers to improve the clarification stage operation and dual media filters. Turbidity and colour levels were 0.1 NTU and <5 HU respectively.

INTRODUCTION

Noosa Heads is a picturesque holiday resort on Queensland's Sunshine Coast in Australia. One of the main incomes for the area is from tourism due to the warm climate, beaches, National Parks and lifestyle. The growth rate for the area is also high as a result.

The provision of high quality drinking water is critical for the continued commercial success of tourism. Due to the increased growth rate, an increase in the capacity of the existing Noosa water treatment plant was required to meet consumer demand.

Noosa Council decided to achieve increased plant capacity, upgrade the plant's ability to address water quality issues and provide high quality drinking water through a DBO contract. CGE Australia was the successful tenderer to supply world's best practice to achieve the Noosa water treatment plant upgrade.

This paper reviews the pilot plant studies undertaken to develop the most effective treatment technology for the Noosa water treatment plant and full-scale plant performance.

WATER QUALITY ISSUES AND CRITERIA

Raw Water

The water sources for Noosa water treatment plant (WTP) include Lake Macdonald and the Mary River. Raw water can be obtained from either source or provided as a mixture from both sources.

The typical values and ranges of water quality are given in Table 1

Table 1 - Raw Water Quality

Parameter	Unit	Typical	Range
Turbidity	NTU	2.75	1- 40
True Colour	HU	22	10- 50
pH	-	6.9	6.4-7.3
Total Manganese	mg/L	0.17	0.05-0.30

During high rainfall events, particularly with Mary River water, the turbidity and true colour can rise significantly.

Treated Water Quality Criteria

Noosa Council established treated water quality criteria to ensure a high quality drinking water. These requirements included levels for some parameters of a higher standard than any known limits worldwide, especially in relation to manganese. They also included limits for new parameters for drinking water in Australia, especially in relation to particle counts. The limit for particle counts, were established to provide a surrogate measure for *Cryptosporidium* and *Giardia* removal.

The key performance criteria are given in Table 2.

Table 2 - Performance criteria

Parameter	Unit	Level
Manganese	mg/L	<0.01
Turbidity	NTU	<0.3
Colour	HU	<5
THMs	µg/L	<50
Particle Counts	counts/ml	<100 or >3 log removal
Taste and Odour	Flavour profile analysis	Effectively remove
Algal Toxins	mouse bioassay test method	Effectively remove

PILOT PLANT STUDIES AND RESULTS

Pilot Plant

The pilot plant was housed in a shipping container and was designed to simulate various treatment processes for inclusion in the Noosa water treatment plant.

This included pre-chemical dosing, clarifier, filters, and the ozone BAC process. Key parameters were monitored and data transferred to a data logger.

Pilot Plant Programme

The pilot plant study evaluated a number of key processes:

- manganese removal with potassium permanganate and pre-chlorination on coated media.

- dual media filters
- polymers as coagulant and filter aids
- ozone BAC process
- ability to meet water quality performance criteria

The pilot plant study period was 3 months from November 1997 to February 1998.

Manganese Removal

The manganese removal process proposed was a multibarrier process to enable the criteria of <0.01mg/L of manganese to be met. This included an upgrading of the Lake Macdonald destratification system, first stage oxidation of soluble manganese using potassium permanganate at elevated pH and final removal and polishing to <0.01mg/L manganese, using pre-chlorination coated media process. The coated media process involves establishing a manganese dioxide coating on the filter media and using chlorine to achieve catalytic oxidation (Craig et al 1993, Craig et al 1997).

This staged manganese removal process would also allow reduced levels of pre-filter chlorination compared to using only the coated media process. This reduced the formation of THMs due to the low chlorine dose and short contact time.

Raw water spiked with soluble manganese up to 0.44mg/L and as well, natural raw water manganese up to 0.26mg/L were tested in the pilot plant.

Potassium permanganate on its own could not achieve the performance criteria of <0.01mg/L. However, the combination of potassium permanganate and pre-filter chlorination on coated media achieved levels of <0.01mg/L and on optimised runs levels <0.005 mg/L. Results are presented in Figure 1 and Figure 2 below.

Final THM levels after ozone BAC process and chlorination were less than the 50 µg/L performance criteria with levels typically <30 µg/L.

Ozone Biologically Activated Carbon (BAC) Study

The process of ozone and BAC was selected to achieve the following outcomes:

- reduced THM levels,
- taste and odour removal,
- algal toxin removal,
- high microbiological performance,
- reduced turbidity, colour and particle counts,

and provide a continuous multibarrier approach to achieve performance criteria. Ozonation would also provide a high level of inactivation of *Cryptosporidium* and *Giardia*.

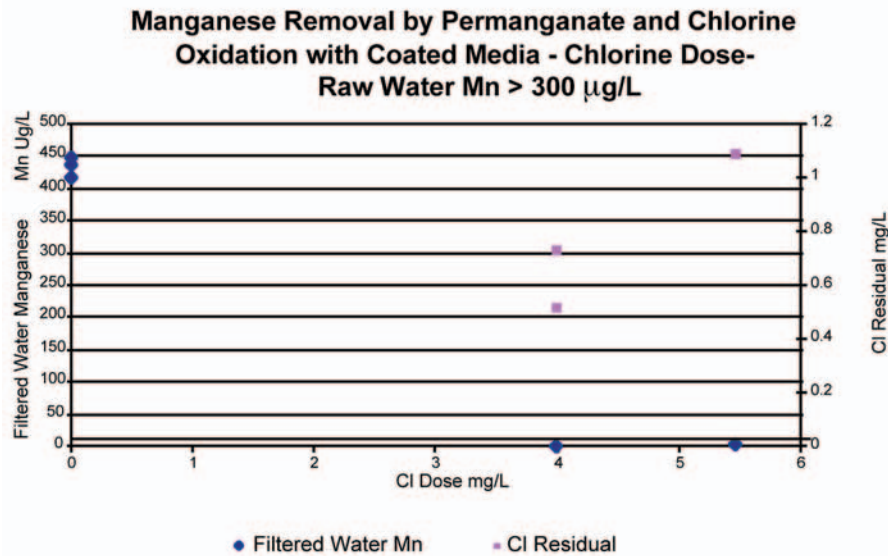


Figure 1 Manganese removal Mn >300 µg/L

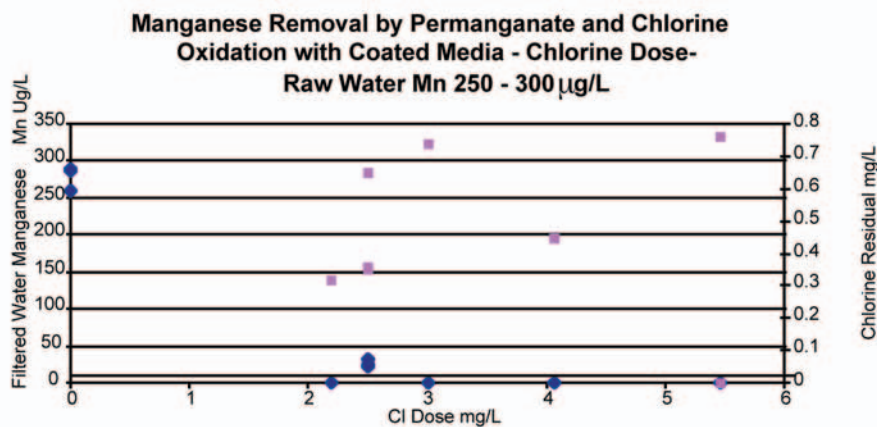


Figure 2 Manganese removal Mn 250-300 µg/L

The ozone BAC advanced technology is used in Europe to provide high quality drinking water, remove pesticides, improve distribution system performance and reduce disinfection byproducts. The activated carbon was Picabiol carbon which has been used in plants in Paris for over 10 years in the BAC process. The biological activity on the activated carbon takes 2-4 weeks to establish. At this stage the performance can be evaluated of the BAC process.

Once the BAC process was established, 20-30% dissolved organic carbon (DOC) removal was achieved. DOC levels were reduced from an average of 3.5 mg/L in the filtered water to 2.4 mg/L in the ozone BAC treated water. Both 10 and 15 minutes BAC empty bed contact time (EBCT) was studied. Generally 5-10% higher DOC removal was obtained with 15 minutes EBCT compared to 10 minutes EBCT.

Final THM levels following the ozone BAC process and chlorination were <30 µg/L with bromate levels <0.02 mg/L. THM levels from the existing water treatment plant were approximately 90 µg/L with THM formation potential approximately 200 µg/L.

Taste and odour problems were evident during the pilot plant study in treated water from the existing water treatment plant. Analysis for taste and odour compounds indicated MIB levels of 10-26 ng/L and geosmin levels of 4-11 ng/L in the raw water. The water supply experienced an earthy musty taste and odour.

After treatment with ozone BAC in the pilot plant, geosmin and MIB levels were <1 ng/L for 10 minutes EBCT, geosmin <1 ng/L for 15 minute EBCT and MIB <5 ng/L for 10 minute EBCT (Figure 3). Taste and odour threshold levels for MIB and geosmin are approximately 10 ng/L.

Cyanobacteria toxins have been shown to be removed effectively in previous studies with the ozone BAC process (Craig et al 1998) with rapid removal in the ozonation stage.

Particle Removal

Particle counting criteria was established to achieve a process that will provide high removal efficiency for *Cryptosporidium* and *Giardia*. Studies were undertaken on

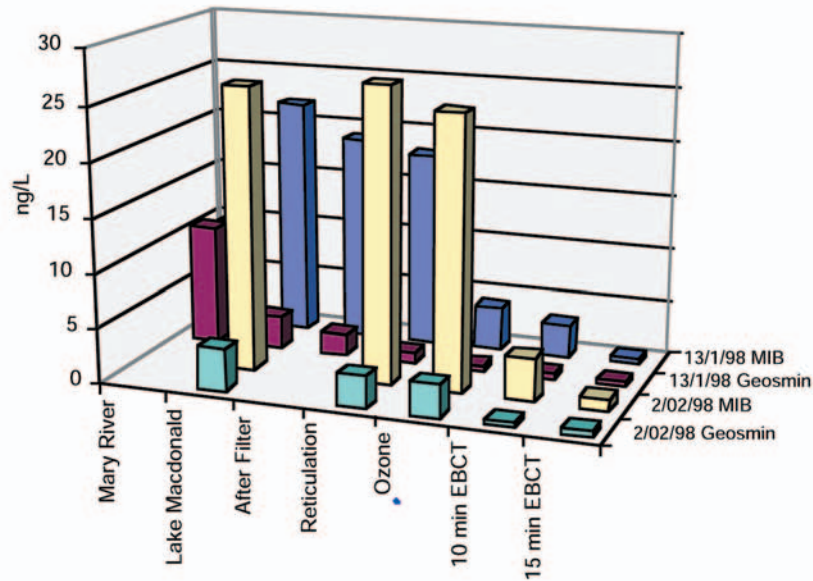


Figure 3 Taste and odour removal

the pilot plant using Met I and Hiac Royco laboratory particle counters.

The removal through the whole treatment train was studied. Particle counts on optimised runs were <50 counts/ml in 3-150 μm size range. This removal was achieved with the addition of a coagulant aid before the clarifier, pre-filter chlorination (used for coated media process), the use of dual media filters of sand and Australia filter coal in place of mono media sand filters and finally the ozone BAC process.

A balance tank was installed in the plant upgrade to provide a constant pumped flow to the ozone BAC process. This will minimise flow variations and changes in particle counts. A period of filter to waste was provided for the BAC filters. This will reduce particle levels that can be associated with the initial filter start up period. On-line particle counters for raw, filtered and treated water will monitor particle levels and log removal of particles.

This was the first time particle counting had been used in Australia as a performance criteria for treated water.

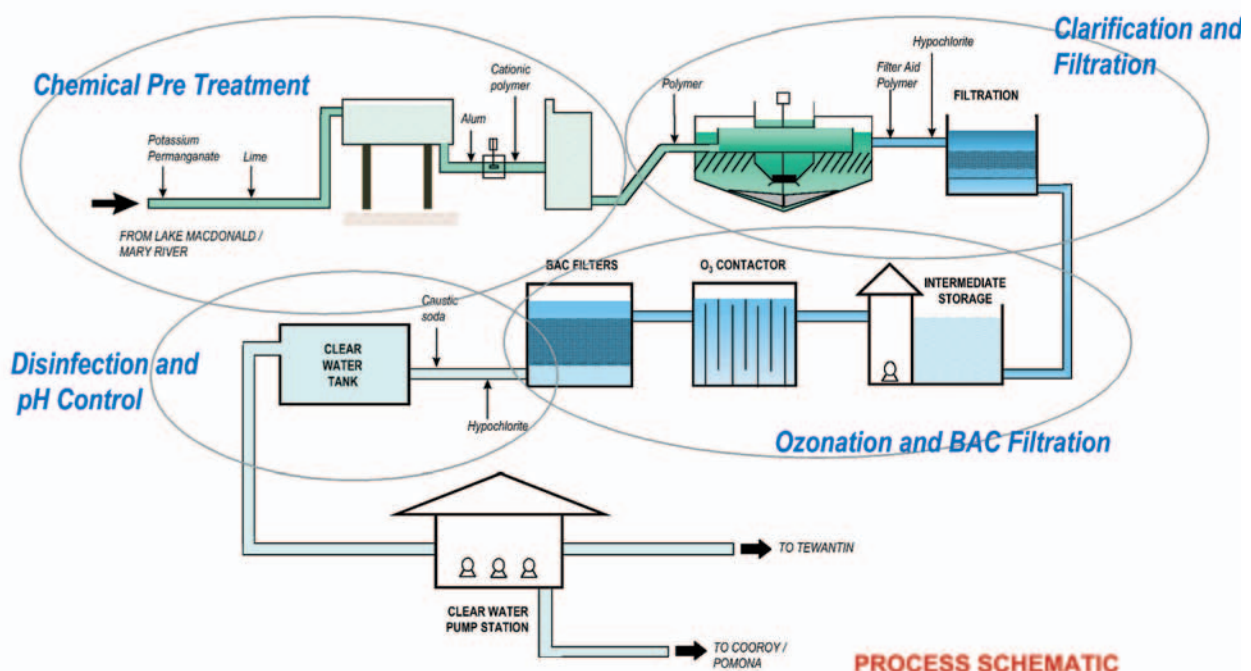


Figure 4 Process upgrade schematic

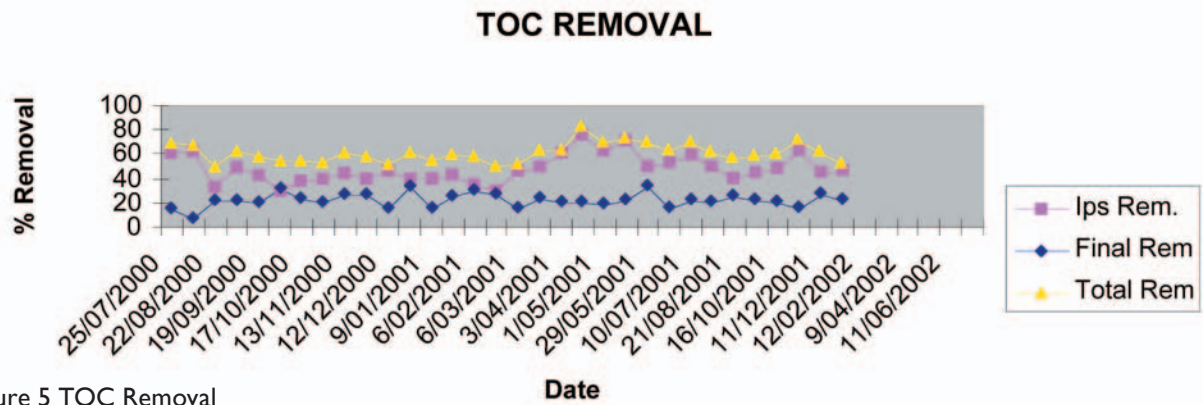


Figure 5 TOC Removal

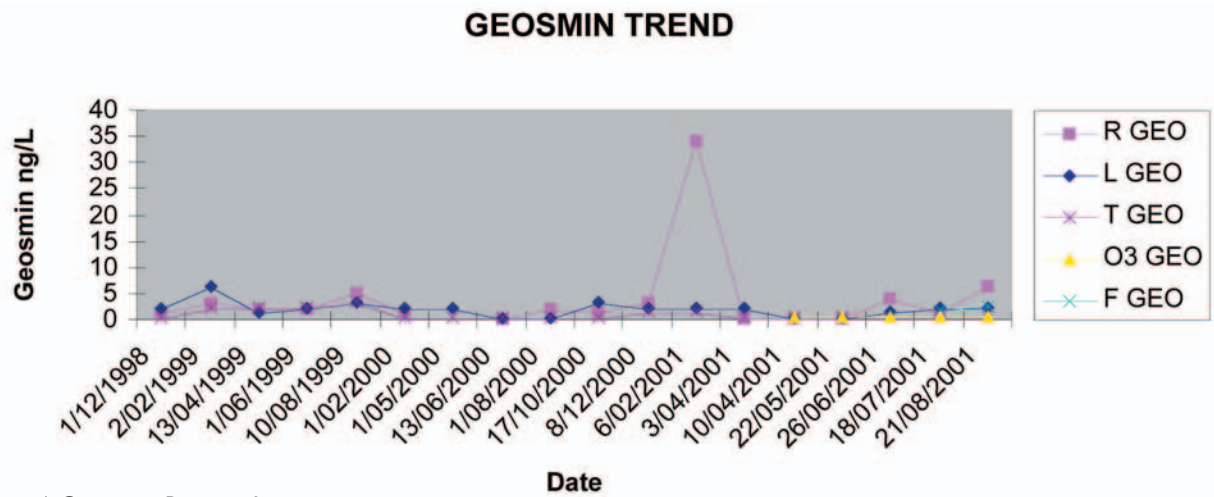


Figure 6 Geosmin Removal

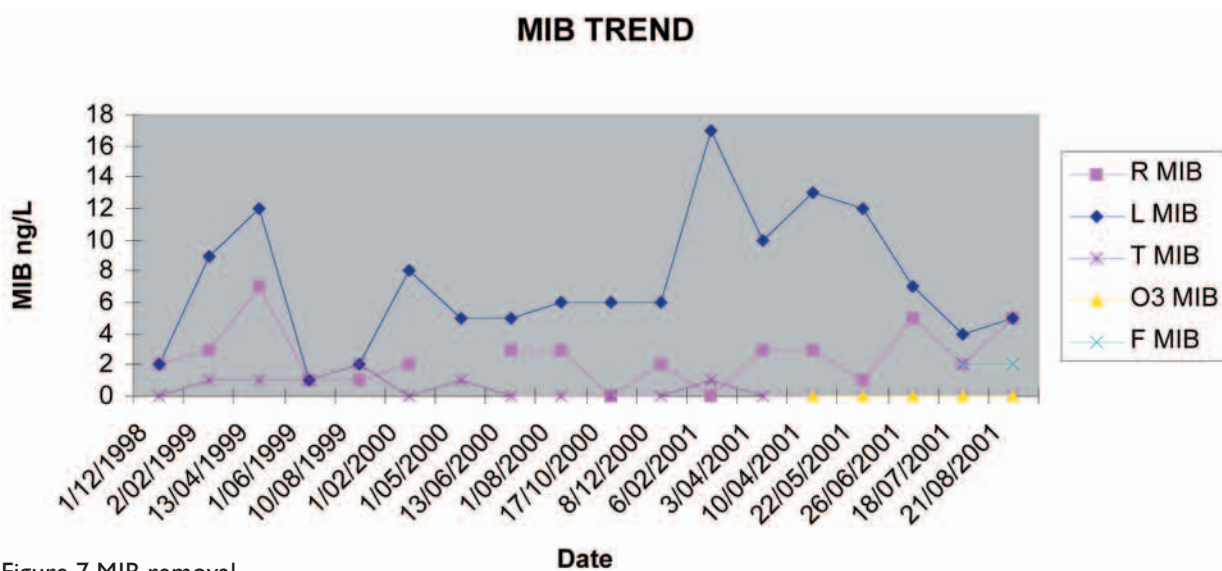


Figure 7 MIB removal

Plant upgrade

The plant upgrade to increase capacity and achieve high treated water quality targets was achieved by:

- plant capacity
- provision of cationic polymer
- coagulant and polymer
- filter aid polymer
- installation of dual media filters
- ultimately a high rate clarifier and further dual media filter
- destratification
- potassium permanganate addition at high pH
- increased contact time
- in-line alum mixer
- provision for cationic polymer
- coagulant aid polymer
- provision for filter aid polymer
- pre-filter chlorination on coated media
- installation dual media in the existing filters
- ozone BAC process
- PLC/SCADA upgrade
- On-line monitoring equipment

FULL SCALE PLANT OPERATION

The plant operation since commissioning in 1998 has resulted in improved performance achieving high water quality criteria. There has been a significant improvement in the taste and odour of the water as measured by the FPA method, which includes community involvement. Taste and odour removal is outlined in Figures 6 & 7.

The distribution system performance has also been improved due to the lower manganese levels and reduced organics in the treated water and resulting lower chlorine demand in the treated water and more stable chlorine residuals in the distribution system. Organics removal across the plant and ozone BAC process is shown in Figure 5. TOC removal is typically 60% across the plant with 20% TOC and 60% BDOC across the ozone BAC stage.

A high level of manganese removal has consistently achieved through the plant to typically 0.001 to 0.002 mg/L in the treated water despite varying manganese levels up to 0.3 mg/L in the raw water.

CONCLUSION

VWA were able to achieve Noosa Council's strict treated water quality guidelines by an innovative approach, introduction of new technology to Australia and the evaluation of options and the thorough testing of the processes in pilot plant studies.

The upgraded plant included the following key processes to address water quality issues.

Manganese removal with destratification, potassium permanganate oxidation at high pH and contact time, and final polishing with pre-filter chlorination on coated media.

Turbidity, colour and particle reduction using coagulant and filter aid polymers, coagulant mixing, dual media filters and ozone BAC process.

Taste and odour, THM and algal toxin removal with the ozone BAC process.

This has allowed Noosa Council to provide high quality drinking water for the consumers and tourists in an area described as paradise by many visitors. The full scale operations have confirmed pilot plant results and achieved improved performance for the distribution system through a continuous multistage advanced treatment process.

REFERENCES

- Bishop S and Bourbigot M-M (1996) Meeting the Proposed Regulations Using Ozone and Biologically Active Carbon New England Water Works Association, Vol CV, No1, pp 1 – 12.
- Craig K, Naylor R, Waite D, Roddy S (1993) Manganese Removal from Sydney Waters Using Manganese Oxide Coated Media Filter Pre-chlorination Proceedings of 15th Federal Convention, AWWA, Vol 4, pp 1065 – 1070.
- Craig K, Bailey D (1995) Cyanobacteria Toxin Microcystin 'LR' Removal Using Activated Carbon - Hunter Water Experience Proceedings 16th Federal Conference, AWWA, Vol 1, pp 579 - 586.
- Craig K, Murray B, Hamilton G, Waterhouse K (1997) Upgrading of a Conventional Water Treatment Plant by Conversion to Contact Filtration Proceedings of 17th Federal Convention, AWWA.
- Craig K, Bowen B, Majerowski A (1998) The Removal of NOM and Algal Toxins Using Ozone Biologically Activated Carbon Under Australian Conditions Watertech Conference, AWWA.
- Waite T, Zaw M, Naylor R, Craig K, Nicholson C (1993) Laboratory and Pilot Plant Studies of Manganese Removal by Potassium Permanganate Oxidation Proceedings of 15th Federal Convention, AWWA, Vol 4, pp 1075 – 1080.

OPTIMISING THE APPLICATION OF PAC TO SUCCESSFULLY REMOVE TASTE, ODOURS AND ALGAL TOXINS IN THE WATER TREATMENT PROCESS

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ABSTRACT

Blooms of cyanobacteria (blue-green algae) in reservoirs produce numerous metabolites during their life cycle. Some of these compounds impart an unpleasant taste and odour, while others are toxic if consumed. The presence of 2-methylisoborneol (MIB) and geosmin in potable water can result, even at low ng/L levels, in unpleasant musty-earthy tastes and odours. The most common type of algal toxins produced by cyanobacteria are the hepatotoxic microcystins, which are a concern as they can cause liver damage and have been identified as tumour promoters. These compounds are not removed by conventional water treatment practice (coagulation/flocculation/sedimentation/filtration). Powdered activated carbon (PAC) is often considered as a treatment option for the removal these compounds as it can be very effective and easy to apply. The success of PAC depends on the application of a sufficient dose which will depend on water treatment plant (WTP) conditions (flow rate and hence contact time), concentration of target compounds and the inlet water quality, particularly the natural organic matter (NOM) concentration and character. This makes the process of determining the optimum PAC dose quite difficult. The aim of the work presented here was to make this process much easier. To do this a mathematical model was fitted to adsorption data for MIB, geosmin, microcystin-LR (mLR) and microcystin (mLA) and adsorption experiments were conducted for each compound in waters of varying NOM character and concentration.

INTRODUCTION

Cyanobacterial blooms in source waters used to produce potable water are of concern as they can produce some compounds that are aesthetically unpleasant and others that are potentially toxic if consumed. Musty-earthy taste and odours produced by many species of cyanobacteria have been identified as 2-methylisoborneol (MIB) and geosmin. These are low molecular weight volatile tertiary alcohols whose presence in treated water even at low ng/L levels can result in consumer complaints.

The most common type of algal toxins produced by cyanobacteria are the hepatotoxic microcystins which have been found to occur in water sources world wide. In Australia the main source of microcystins is from the cyanobacterium *Microcystis aeruginosa*. Microcystins consist of seven amino acids, with the terminal amino acids joined to form a cyclic compound. More than

60 different hepatotoxic microcystins have been characterised (Sivonen and Jones, 1999). Clinical signs of hepatotoxicosis have been observed in field poisonings involving cattle, sheep, horses, pigs, ducks and other wild and domestic animals (Carmichael, 1992), and have been implicated as the major cause of death of dialysis patients in a clinic in Caruaru, Brazil in 1996 (Pouria *et al* 1998). Microcystin removal in the water treatment process is essential for the production of safe drinking water.

These compounds are not removed by conventional water treatment practice (coagulation/flocculation/sedimentation/filtration). Powdered activated carbon (PAC) is often considered as a treatment option for the removal these compounds as it can be very effective and easy to apply. The success of PAC depends on the application of a sufficient dose which will depend on water treatment plant (WTP) conditions (flow rate and hence contact time), concentration of target compound(s) and the inlet water quality, particularly the NOM concentration and character. If the effect that each of these factors has on PAC dose can be accounted for, the process of using PAC will be much more efficient. To do this the homogeneous surface diffusion model (HSDM) was used to predict the adsorption kinetics of MIB, geosmin, mLR and mLA. The HSDM has been successfully applied to predict the adsorption of musty-earthy tastes and odours onto PAC (Huang *et al.*, 1996; Gillogly *et al.*, 1998; Cook *et al.*, 2001). The information gained from the HSDM can be used to predict the PAC dose required to remove these compounds for a range of contact times and initial concentrations. A drawback of the HSDM is that it is only applicable to the water that the tests were carried out in, hence changes in water quality (NOM concentration and character) could result in inaccuracies in the predictions. Adsorption experiments were completed in a range of waters with the data analysed to determine if the amount adsorbed could be related to the water quality parameters of dissolved organic carbon (DOC), UV absorbance at 254 nm, and colour.

MATERIALS AND METHODS

Water Samples

Water samples obtained were filtered through a 0.2 µm cartridge filter and stored at 4 °C until used.

Powdered Activated Carbon

All PACs were dried at 105 °C for 24 hours then cooled and stored in a desiccator before use. For the mLR and

mLA adsorption experiments a chemically activated wood based carbon was used while for the MIB and geosmin experiments, a coconut-based steam activated carbon was used.

Microcystins

Microcystin LA and LR were isolated from a natural bloom of *Microcystis aeruginosa* that occurred in South Australia over the summer of 1998-99. The bloom produced an approximate 50/50 mix of mLR/mLA with some other minor unidentified analogues also present. This mixture was used in the PAC adsorption experiments. The presence of mLR and mLA was confirmed by liquid chromatography-mass spectrometry. Microcystin YR was supplied by Calbiochem, catalogue number 475819, Nodularin was supplied by BioMol catalogue number EI-194 and Microcystin RR, Microcystin LW and Microcystin LF were supplied by Alexis with catalogue numbers 350-043-C100, 350-080-C025 and 350-081-C025 respectively.

EXPERIMENTAL PROCEDURES

Kinetic studies

mLR and mLA

Raw water was spiked with microcystin and 700 mL portions were added to 2 litre acrylic jars with each portion representing a different contact time with PAC. PAC (pre-wetted overnight in deionised water) was added to samples mixed at 100 rpm on a six-paddle gang stirrer. PAC contact time was between 10-120 minutes. Prior to analysis, samples were filtered through 0.45 μm membrane filters to remove the PAC.

MIB and geosmin

MIB or geosmin was added to a constantly stirred raw water sample (2 litres). After 15 minutes of mixing a sample was taken to determine the initial concentration. PAC was added and samples were taken at predetermined intervals over the following four hours. Samples were pressure filtered through 0.45 μm disposable filters to remove the PAC.

Predicting adsorption using the HSDM

The HSDM was used to predict the kinetics of MIB, geosmin, mLR and mLA adsorption. This was performed according to the method described by Cook *et al.* (1999). A detailed explanation of the HSDM is given elsewhere (Najm *et al* 1991; Traegner and Suidan, 1989).

Analytical Methods

DOC was determined with a total organic carbon analyser (Sievers Instruments Inc. Model 820), UV absorbance at 254 nm was measured using a UV/VIS spectrophotometer (GBC Model 918) with a 1cm quartz cell and colour was determined as described by Bennett and Drikas (1993). Microcystin analysis was carried out as outlined by Rositano (1996) while geosmin was analysed using solid phase microextraction-gas chromatography/mass spectrometry (SPME - GC/MS) and MIB (^{14}C -labelled MIB) was analysed using a liquid scintillation counter (Beckman LS3801)

RESULTS AND DISCUSSION

Predicting the Adsorption of Problematic Algal Metabolites

The HSDM has been applied to predict the adsorption of MIB and geosmin from the inlet waters to four Adelaide metropolitan WTPs and has been shown under most circumstances to predict the removal of MIB and geosmin in laboratory tests (Cook *et al* 2001). Figure 1 shows experimental data and HSDM fit and prediction of batch kinetic data for MIB and geosmin removal from Anstey Hill WTP inlet water. The bold line shows the HSDM fit to kinetic data to determine parameters for the application of the model, equilibrium adsorption data (not shown) is also required. These parameters are then used to predict adsorption for different conditions such as initial concentration and PAC dose as shown by the dotted line. Application of HSDM predictions to historical data of geosmin removal at four Adelaide metropolitan WTPs showed that the HSDM could predict geosmin removal through the plants ($r=0.86$) (Cook *et al* 2000). This model was applied to the

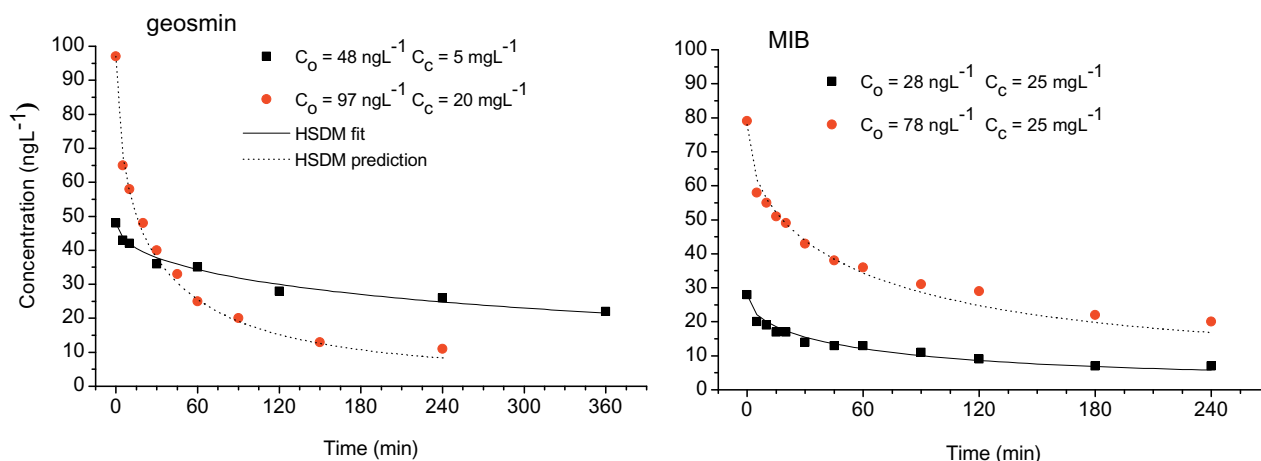


Figure 1 HSDM fit and prediction for the adsorption of MIB and geosmin

adsorption of two microcystin analogues, mLR and mLA. Figure 2 shows that the HSDM is also applicable for the larger toxin molecules and that the fraction remaining is independent of initial concentration and is predicted by the HSDM. Several researchers have found this trend for musty-earthly taste and odours and atrazine at concentrations applicable to water treatment (Gilligly *et al* 1998; Knappe *et al* 1998; Graham *et al* 2000; Cook *et al* 2001). Using the HSDM allows us to predict PAC doses for the removal of problematic compounds.

Table I shows predicted PAC doses for the reduction of mLR and mLA to $1 \mu\text{gL}^{-1}$ which is below the Australian Drinking Water Guideline value of $1.3 \mu\text{gL}^{-1}$ as mLR toxicity equivalents (NHMRC/ARMCANZ, 2001). The values in the table highlight the effect of increase in inlet toxin concentration and contact time on PAC dose and more importantly the significant difference in the amount of PAC needed to effectively control both compounds. For the PAC tested, generally twice as much PAC is needed to remove mLA compared with mLR. This difference has also been noticed for other PACs.

Table I Predicted PAC doses for the removal of mLR and mLA to $1 \mu\text{gL}^{-1}$

Initial toxin concentration ($\mu\text{g L}^{-1}$)	mLR		mLA	
	Contact time (min)			
	30	60	30	60
	PAC dose mg L^{-1}			
2	13	10	35	26
4			>50	41
8			>50	50

Effect of NOM on Adsorption

The adsorption of mLR, mLA, MIB and geosmin was tested in a range of waters of varying NOM concentration and character. The waters tested are shown in Table 2 and were selected to represent a range of water qualities that could be encountered. Most waters were sampled from surface waters while one was treated with a magnetic ion exchange resin (MIEX®). F5DAX8 and F2DAX8 are high (>30000 dalton) and low (500-1000 dalton) molecular weight NOM fractions that were isolated by Hepplewhite (2000).

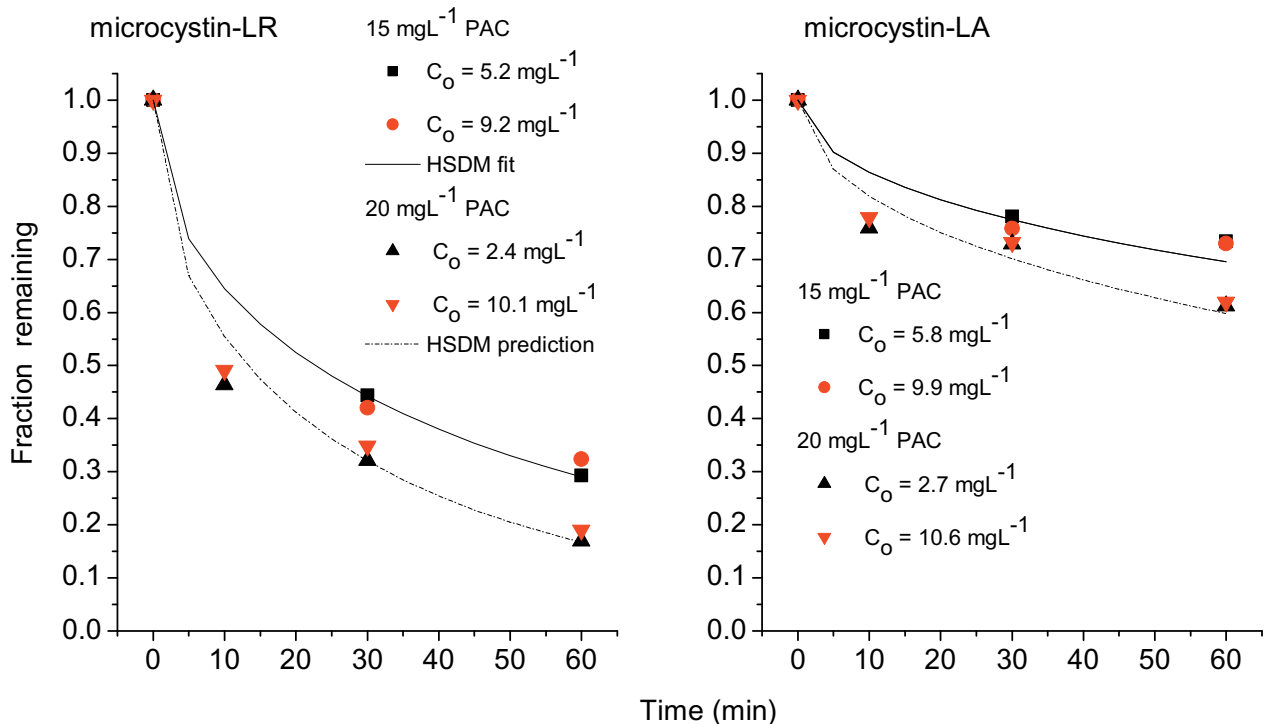


Figure 2 HSDM fit and prediction for the adsorption of mLR and mLA from River Murray water (Mannum, DOC = 6.7 mgL^{-1})

Figure 3 shows that there was no direct relationship between MIB and geosmin adsorption and the parameters measured. There was a general increase in MIB and geosmin remaining in solution with an increase in each of the parameters but as shown this can not always be relied upon.

Table 2 Waters tested to examine the effect of NOM on adsorption

Water	DOC (mgL ⁻¹)	UV Absorbance @ 254 nm (cm ⁻¹)	Colour (HU)
Lock 3 (MIEX [®] treated)	1.9	0.021	2
Landers Shute*	3.1	0.056	7
Glenorchy Channel	3.9	0.117	24
F5 DAX8*	4.8	0.251	60
F2 DAX8*	4.9	0.200	22
Lock 3 (R. Murray)	6.2	0.125	12
Mannum (R. Murray)*	6.7	0.146	12
diluted Myponga*	6.9	0.268	42
Lake Fyans	7.8	0.188	34
Happy Valley	8.8	0.229	31
Hope Valley	9.9	0.339	58
Happy Valley* [^]	10.0	0.361	61
Myponga*	13.2	0.524	86

* Used for MIB and geosmin adsorption experiments

MIEX[®] is a registered trademark of Orica Australia Pty Ltd.

[^] not used for mLR and mLA adsorption experiment

Unlike MIB and geosmin there was a good correlation between the percent toxin remaining and DOC and UV absorbance at 254 nm (Figure 4). Linear regression analysis of the data showed that DOC was a better predictor for mLR adsorption (correlation coefficient (R) = 0.89) than UV absorbance at 254 nm (R = 0.78) and colour (R = 0.25) while for mLA the opposite was found (DOC, R = 0.77, UV absorbance at 254, R = 0.95 and colour, R = 0.87).

Changes in NOM concentration and character affected the adsorption of MIB and geosmin differently compared with mLR and mLA. This is most likely due to the size of the target compounds in question and those that compete for adsorption sites on the activated carbon. For MIB it has been found that compounds of similar size compete most strongly for adsorption sites (Newcombe *et al.*, 1997). The concentration of these low molecular weight compounds may change considerably with little resultant effect on the water quality parameters measured. For the microcystins direct competition may exist with larger compounds and that changes in the concentration of these compounds can be noticed with determination of the bulk water quality parameters of DOC and UV absorbance at 254.

Due to the differences in adsorption of mLR and mLA, other microcystin analogues were also studied. Figure 5 shows that the amount of toxin remaining increased with an increase in the DOC and that there was considerable variation in the adsorption of the various analogues with the ease of removal in the order: mRR > mYR > mLV = nodularin = mLR > mLF > mLA. This result highlights the fact that to effectively use PAC to remove microcystins with PAC the analogue(s) present need to be identified. Further investigation is being conducted to explain this adsorption behaviour. By understanding the importance of the distinguishing amino acid group of each analogue has in adsorption, predictions could be made about the

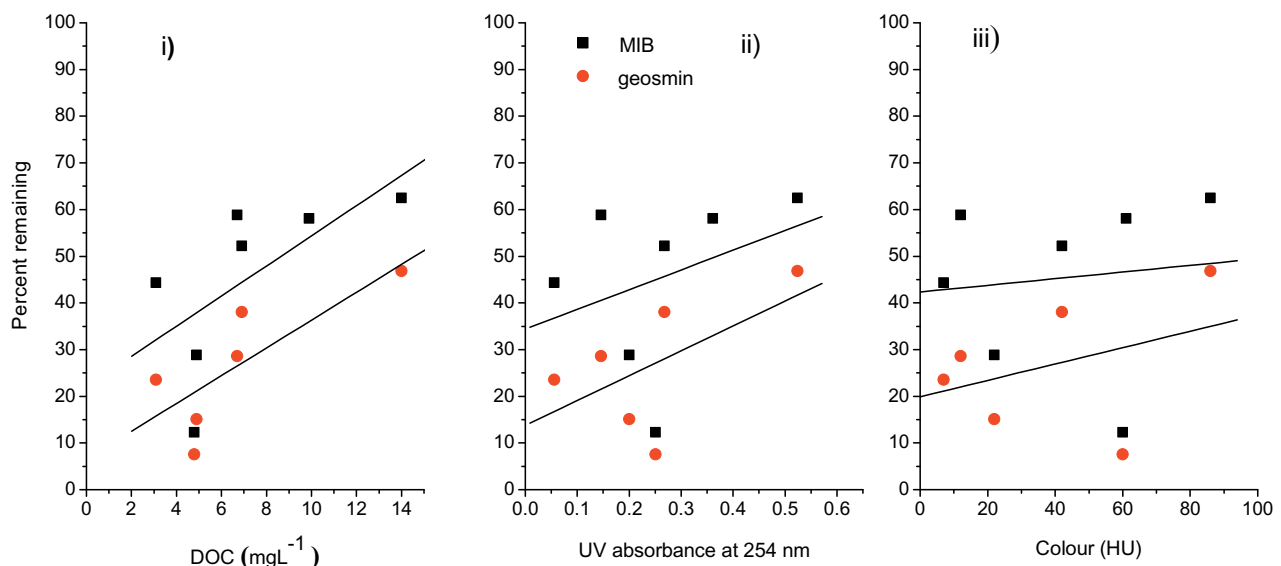


Figure 3 Relationship between percent MIB and geosmin remaining and water quality after treatment with 15 mgL⁻¹ PAC for 30 minutes i) DOC, ii) UV absorbance at 254 nm, iii) Colour

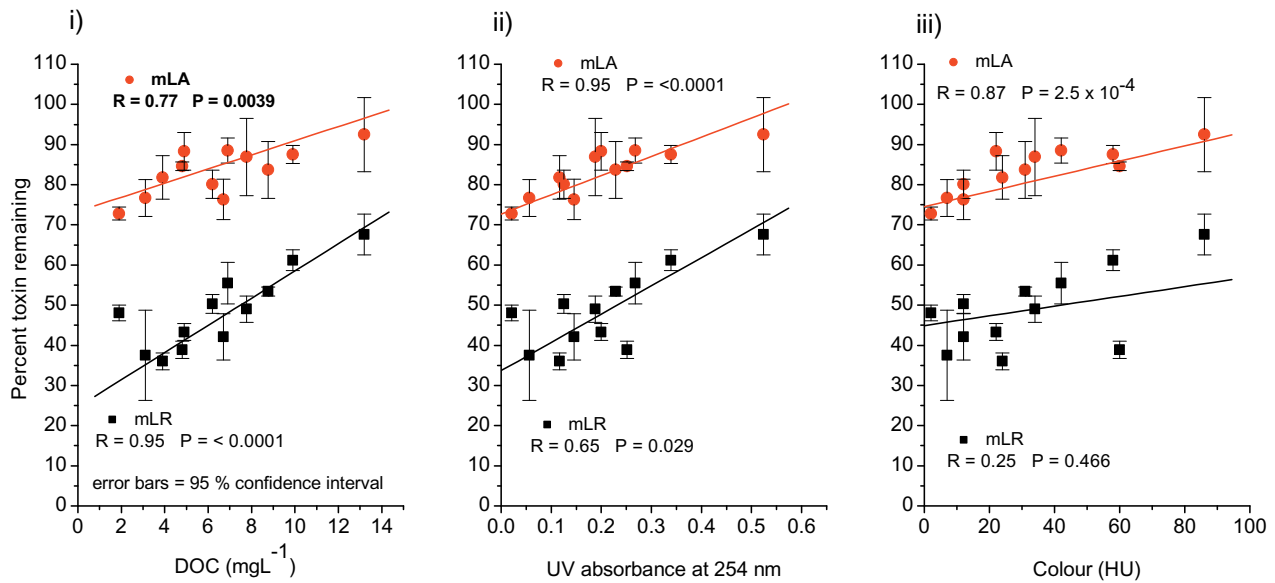


Figure 4 Relationship between percent mLR and mLA remaining and water quality after treatment with 15 mgL⁻¹ PAC for 30 minutes i) DOC, ii) UV absorbance at 254 nm, iii) Colour

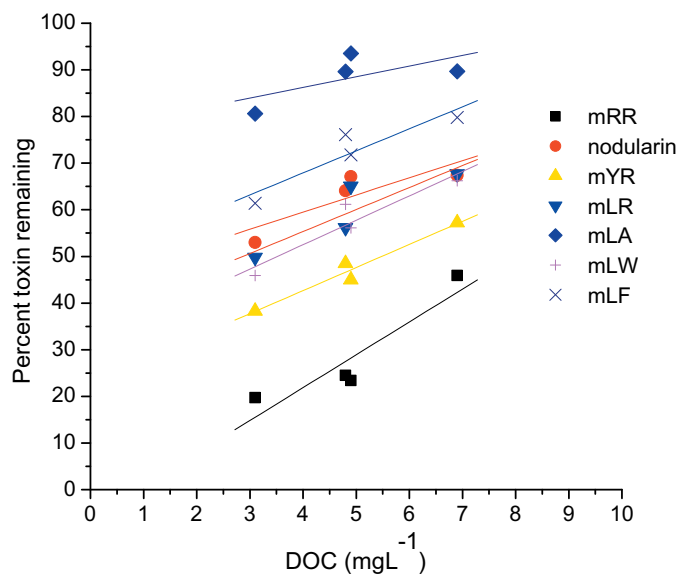


Figure 5 Adsorption of various microcystin analogues after 10 minutes with 15 mgL⁻¹ PAC (Initial toxin concentration = 2-3 µgL⁻¹)

adsorption of other analogues not yet studied and also allow the modification of adsorbents to target particular analogues.

CONCLUSION

The adsorption of MIB, geosmin, mLR and mLA onto PAC can be successfully predicted using the HSDM. Changes in NOM concentration and character affected the adsorption of MIB and geosmin differently compared with mLR and mLA. The adsorption of mLR and mLA was significantly different with mLR much more easily removed than mLA. Subsequent testing of other microcystin analogues also showed differences in adsorption efficiency. Overall this work showed that the application of PAC can be optimised by using

mathematical modelling to predict PAC doses. For the adsorption of microcystins this work highlights that adsorption behaviour could be related to changes in water quality as measured by DOC and for the effective use of PAC the microcystin analogue of concern needs to be identified.

REFERENCES

- Bennett LE and Drikas M (1993) The evaluation of colour in natural waters. *Wat. Res.* 27(7), pp 1209-1218.
- Carmichael WW (1992) Cyanobacterial secondary metabolites – The cyanotoxins. *J. Appl. Bacteriol.*, 72, pp 445-459.

- Cook D, Newcombe G, Kaeding U and Sztajn bok P (2000) Treating tastes and odours: Is the "wait and see" method the best approach for choosing activated carbon doses? *Proceedings of the New Zealand Water and Waste Water Association 42nd Annual Conference and Expo 27-29 September, Rotorua, New Zealand.*
- Cook D, Newcombe G and Sztajn bok P (2000) The application of powdered activated carbon for MIB and geosmin removal: predicting PAC doses in four raw waters. *Wat Res.* 35(5), pp1325-1333
- Gillogly TET, Snoeyink VL, Elarde JR, Wilson CM and Royal EP (1998) ¹⁴C-MIB adsorption on PAC in natural water. *J. Amer. Water Works Assoc.* 90,1, pp 98-108.
- Hepplewhite C (2000) The Isolation, Fractionation and Characterisation of NOM from water and its effect on the adsorption of taste and odour compounds by activated carbon. University of South Australia, Australia, Ph.D. thesis.
- Huang C, Van Benschoten JE and Jensen JN (1996) Adsorption kinetics of MIB and geosmin. *J. Amer. Water Works Assoc.* 88,4, pp 116-128.
- Knappe DRU (1996) Predicting the removal of atrazine by powdered and granulated activated carbon. Doctoral dissertation, Univ. of Illinois-Urbana.
- Najm IN, Snoeyink VL, Galvin TL and Richard Y (1991) Control of organic compounds with powdered activated carbon. AWWARF (90581), Denver.
- Newcombe G, Drikas M and Hayes R (1997) Influence of characterised natural organic material on activated carbon adsorption: II. Effect on pore volume distribution and adsorption of 2-methylisborneol. *Wat. Res* 31 (5) pp 1065 1073.
- NHMRC/ARMCANZ (2001) Australian drinking water guidelines, fact sheet sheets – Micro-organisms 3: Toxic Algae fact sheet 17a microcystins.
- Pouria S, de Andrade A, Barbosa J, Cavalcanti RL, Barreto VTS, Ward CJ, Preiser W, Poon GK, Neild GH and Codd GA (1998) Fatal microcystin intoxication in haemodialysis unit in Caruaru, Brazil. *The Lancet.* 352, July 4, pp 21-26.
- Rositano J (1996) The destruction of cyanobacterial peptide toxins by oxidants used in water treatment. Urban Water Research Association Australia, Research Report No 110, Melbourne.
- Sivonen K and Jones G (1999) *Cyanobacterial Toxins*. In Chorus, I. and Bartram J. (eds) Toxic cyanobacteria in water: A guide to their public health consequences, monitoring and management. E & FN Spon Publishing, London, pp 41-111.
- Traegner UK and Suidan MT (1989) Parameter evaluation for carbon adsorption. *J. Envir. Engrg., ASCE*, 115, 1, pp 109-128.

INVESTIGATIONS INTO THE REMOVAL OF *C. RACIBORSKII* CELLS AND CYLINDROSPERMOPSIN FROM DRINKING WATER USING BIOLOGICAL ACTIVE FILTERS

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This paper represents part of the PhD thesis of Ms Maree Smith.

INTRODUCTION

Australia currently has no drinking water guidelines for the cyanotoxin cylindrospermopsin (CYN) and given the growing concerns about non lethal and chronic effects of this toxin it is of great importance that water treatment processes are employed to reduce CYN to a level deemed not to be a hazard to human health.

Removal of CYN from contaminated water storages presents various technical challenges for water utility managers. Firstly, the removal of cyanobacterial cells which contain the majority of toxin and secondly, the removal of highly water-soluble toxin that may leak from cells during growth or be released when the cyanobacterial cells lyse.

Biologically active filtration systems (BAF) have the potential to offer cheap and effective water treatment processes which have previously demonstrated removal of cyanobacteria and associated soluble cyanotoxins.

AIMS

This study aims to investigate the ability of biologically active filters to remove *C. raciborskii* cells and soluble CYN. A BAF pilot plant was used to simulate the processes of water treatment during a natural toxic cyanobacterial bloom situation and provided quantitative data on the effect of the processes on *C. raciborskii* and associated CYN.

MATERIAL AND METHODS

Biologically Active Filtration Pilot Plant Located at North Pine Dam, Brisbane, QLD, Australia

The biologically active slow sand filtration pilot plant is located at North Pine Dam (NPD), Brisbane, Queensland, Australia. NPD is located near Petrie just north of Brisbane, Queensland and is owned and managed by the Southeast Queensland Water Corporation. The dam was constructed in 1974 and has a storage capacity of 215,000 megalitres and an average

depth of ten metres. Water is drawn directly from NPD by Brisbane City Council for treatment and distribution to the northern areas of Brisbane City, parts of Pine Rivers Shire and Redcliffe City.

The plant consisted of a reservoir holding tank in which water pumped from NPD was held and gravity fed into a biologically active roughing filter. The roughing filter (RF) was 5m X 0.5m long and 1m in depth and consisted of filter materials that successively reduced in size (approx. 20 mm, 10 mm and 5 mm). The dam water passed through the RF and then through a biologically active sand filter. The slow sand filter (SSF) was 1.6 m X 1.6 m wide and 2.4 m in depth. The water flowed through the plant at a rate of 8 L hr⁻¹ with a contact time of approximately six hours. The plant was running for a period of approximately twelve months before analysis begun. This period of time was used to ensure that the filter became colonized with CYN degrading bacteria and to ensure that a toxic bloom of *C. raciborskii* occupied the dam. The plant was designed and constructed by Queensland Department of Natural Resources and Mines and kindly donated to Queensland Health Scientific Services (QHSS) and National Research Centre for Environmental Toxicology (EnTox) for this study. The aggregate located in the RF was supplied by River Sands PTY LTD, Carbrook, QLD, Australia and the sand located in the SSF was supplied by Queensland Cement Distributors, Coopers Plains, Brisbane, Australia. The pilot plant was located at NPD as this water storage had a history of toxic *C. raciborskii* blooms with the first being recorded in 1978.

RESULTS

Monitoring of *C. raciborskii* Cells Through a Biologically Active Filtration Pilot Plant

Figure 1 presents the results of *C. raciborskii* counts before and after passage through the plant. The results were represented as *C. raciborskii* cells mL⁻¹. The *C. raciborskii* cell numbers in the NPD raw water source ranged from 5860 to 76000 cells mL⁻¹ during the twelve month experimental period. The highest concentration of cells were detected during September 2002. No whole

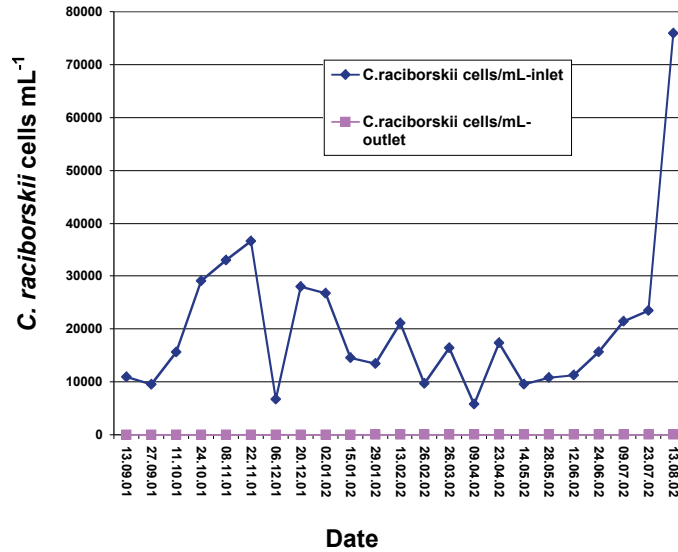


Figure 1. Monitoring of *C. raciborskii* cells through the BAF plant for a period of 12 months.

or fragmented *C. raciborskii* cells were detected using phase contrast microscopy (X 400 magnification) after CYN contaminated NPD water had filtered through the RF and SSF located within the BAF pilot plant. Figure 1 presents the results of *C. raciborskii* identification and enumeration in the NPD raw water prior to filtration.

Monitoring of Total and Soluble CYN through a Biologically Active Filtration Pilot Plant

Total and soluble CYN was totally removed after NPD contaminated raw water passed through the RF and SSF. Figure 2 presents the results of both total and soluble CYN in the NPD raw water prior to filtration and in the treated water post filtration. The results were represented as $\mu\text{g L}^{-1}$ CYN. The levels of total CYN in the NPD raw water source ranged from 0.1 to $3.9 \mu\text{g L}^{-1}$ during the twelve month experimental period. The highest concentration was detected during September 2002. The levels of soluble CYN in the NPD raw water source ranged from 0 to $2.2 \mu\text{g L}^{-1}$ during the twelve-month experimental period.

The highest concentration of total toxin corresponded with the highest concentration of *C. raciborskii* cells. No acclimation or lag phase was evident during the study.

Confirmation of CYN Degrading Bacteria in Biologically Active Filtration Pilot Plant

All aggregate samples taken from the roughing (approx. 5, 10, 20 μm) and sand filter (sand) degraded CYN in approximately 14-20 days implying the presence of CYN degrading bacteria in these aggregates (Figure 3). The concentration of CYN in the control sample remained at 79% of the initial concentration at day 20 of the study.

DISCUSSION

The results of this study demonstrated that after a period of filter ripening (approximately 12 months) a combination of biologically active roughing and slow sand filters mediated complete removal of *C. raciborskii* cells and soluble cyanotoxins during the twelve month experimental period. The cell density and soluble toxin

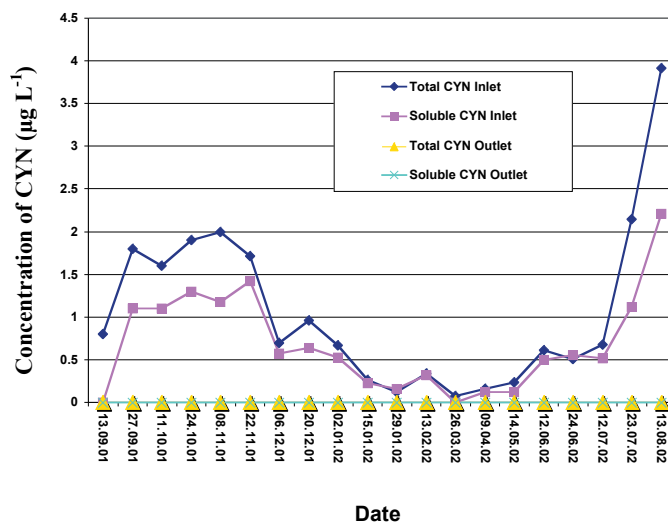


Figure 2. Monitoring of total and soluble cylindrospermopsin through the biologically active filtration plant.

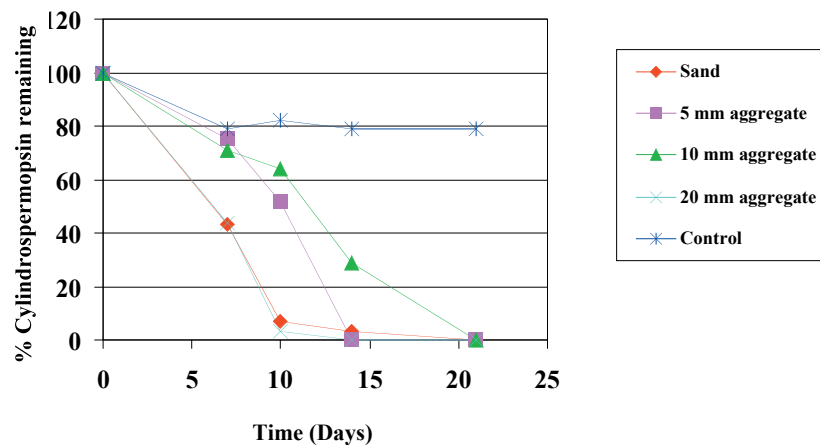


Figure 3. Presence of cyindrospermopsis degrading bacteria in biologically active filtration plant.

concentration during this period ranged from 5860 to 76000 cell mL⁻¹ and 0 to 2.2 µg L⁻¹ respectively.

The most feasible mechanism for the successful elimination of *C. raciborskii* cells in our experiments was physical removal. It was proposed that the *C. raciborskii* cells entered the roughing filter and became entrapped within the gravel matrix as the water flowed horizontally through the compartments. This pretreatment of the source water resulted in either complete elimination of cells or reduced cell concentrations to a suitable level for slow sand filtration. Slow sand filters then retained any remaining traces of *C. raciborskii* cells. Slow sand filters operate at low filtration rates and rely on cake filtration of the filter for particulate straining. As the surface cake develops during the filtration cycle, the cake itself assumes the dominant role in filtration rather than the sand particles themselves.

Sorption processes can play a role in the removal of soluble CYN. During the flow of soluble CYN through both the roughing and sand filter adhesion of the cyanotoxin onto the outer surfaces of the aggregate or biofilm located throughout the filters may have occurred. The cyanotoxin would then have been removed when the aggregate was discarded and replenished during the maintenance procedures.

However, results obtained from this study (not included) indicated that CYN was not significantly adsorbed onto native matrix in both the roughing and slow sand filters. The role of adsorption/absorption of CYN onto any biofilm present in the plant has not been investigated.

CONCLUSIONS.

Results of the studies conducted clearly demonstrated that after a 12 month maturation phase and previous exposure to CYN the BAF pilot plant was effective in eliminating 100% of *C. raciborskii* cells and soluble CYN from naturally contaminated water during the 12 month experimental period. The highest concentration of *C. raciborskii* cells passing through the plant was 76 000 cells ml⁻¹ and the highest concentration of soluble CYN was 2.2 µg L⁻¹. The high elimination efficiency of soluble CYN removal was attributed to biological action and was confirmed with the isolation of CYN degradative organisms from the matrix of both the RF and SSF.

THE ROLE OF BIOLOGICAL FILTRATION IN THE REMOVAL OF ALGAL METABOLITES USING GAC

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EXECUTIVE SUMMARY

While biological removal of contaminants in drinking water is a process that has been utilised in the industry for many years, the full potential has not yet been reached. This is due to the lack of understanding of the many microbiological processes taking place within the biofilm.

Taste and odour compounds 2-methyl isoborneol (MIB) and geosmin, and the group of algal hepatotoxins, the microcystins, are of concern to drinking water suppliers world-wide, and many reports have suggested that the compounds are biodegradable. The removal of dissolved organic carbon (DOC) is also a priority for water suppliers to aid the minimisation of disinfection by-products. The aim of this work was to determine whether the removal of these compounds through granular activated carbon (GAC) filters was predominantly through biological or physical processes, and to increase our understanding of any biological processes taking place within the filter.

The process of biofiltration through GAC, in the presence or absence of pre-ozonation, is not as straightforward as sometimes indicated in the literature. The addition of the ozone step does not always lead to increased removal of DOC. Pre-ozonation may increase the biodegradability of the DOC, depending on the character; however, the process may also reduce the adsorption of DOC, and the two processes are difficult to distinguish in a porous material such as GAC. This also applies to the removal of MIB and geosmin. These compounds are of low concentration, and very low molecular weight compared with the bulk of the DOC, and in a GAC column there is a large surface area available for adsorption. In the absence of evidence, it should not be assumed that removal of these compounds by an "exhausted" GAC is due to biological processes. In contrast, the microcystins tested are not well removed by physical processes in the exhausted GAC, and the onset of biological degradation through the filter is quite clear.

The isolation and identification of microcystin-degrading bacteria colonising GAC biofilters is not a trivial exercise.

The major difficulties associated with the process are:

- Sampling of the GAC from an appropriate part of the column. For example, should samples be taken from the top of the column, or is a mixed sample, comprised of carbon from a range of filter depths, more representative?
- Removing as many bacteria from the surface as possible, without damage
- Isolating bacterial strains through culturing leads to omission of the non-culturable organisms
- Degradation may be due to some unknown synergistic relationship between different bacteria.

INTRODUCTION

While biological removal of contaminants in drinking water is a process that has been utilised in the industry for many years, the full potential has not yet been reached. This is due to the lack of understanding of the many microbiological processes taking place within the biofilm.

Drinking water treatment utilising biological degradation usually takes place on a fixed biofilm on a filter medium; for example, "schmudzdecke" on slow sand filters and biological growth on granular activated carbon filters. There are many advantages to this type of treatment. Biological filter processes generally:

- Are of low technology, requiring relatively little maintenance and are therefore potentially of significant interest to regional and/or remote communities, and less advanced communities in developing countries
- Require relatively low infrastructure and running costs
- Do not require additional treatments and involve processes that remove contaminants without the addition of chemicals that in themselves may have potential, or perceived, health effects, or may produce by-products that are undesirable in drinking water.

Taste and odour compounds 2-methyl isoborneol (MIB) and geosmin, and the group of algal hepatotoxins, the microcystins, are of concern to drinking water suppliers world-wide, and many reports have suggested that the compounds are biodegradable (Jones *et al.* 1994; Tanaka *et al.* 1996; Saadoun and Elmigdad 1998). These algal metabolites are therefore ideal target compounds for a study of biofiltration. The removal of dissolved organic carbon (DOC) is also a priority for water suppliers to aid the minimisation of disinfection by-products. The aim of the work reported here was to determine whether the removal of these compounds through granular activated carbon (GAC) filters was predominantly through biological or physical processes, and to increase our understanding of any biological processes taking place within the filter.

MATERIALS AND METHODS

Materials

Geosmin and MIB (99.9%) were supplied by Ultrafine Chemical Industries Ltd. All other chemicals used were analytical grade. Microcystin LR (>98% by HPLC) was obtained from Sapphire Bioscience (Sydney, Australia).

Sterilisation

Three methods were used for the sterilisation of the preloaded GAC

- Sonication for 30 minutes in a sonicator bath (Unisonics Pty Ltd)
- Drying by rotary evaporation to constant weight
- Disinfection by the addition of 100 mg L⁻¹ of sodium azide

MIB and Geosmin Analysis

Geosmin and MIB were analysed using solid phase microextraction - gas chromatography/mass spectrometry (SPME - GC/MS).

Microcystin Analysis

The samples were analysed by HPLC with PDA detection at 240 nm. Quantification of microcystin LR and microcystin LA was by direct comparison of peak area with an external standard of microcystin LR. Microcystin LA was identified using LC MS.

Dissolved Organic Carbon Analysis

Dissolved organic carbon (DOC) was measured using a Seivers 820 Total Organic Carbon Analyser.

Pilot Plant

Further details of pilot plant trials can be found in Newcombe (2002b).

Laboratory Scale GAC Experiments

Granular activated carbon samples from the Myponga pilot plant were removed from the filter and placed in a glass laboratory column (2.5 cm diameter, 12 cm bed depth). Water was pumped through the column at a flow rate to allow an empty bed contact time of 15 minutes.

RESULTS AND DISCUSSION

Dissolved Organic Carbon Removal

In the literature it is often suggested that once GAC is "exhausted" for DOC removal any removal of other contaminants through the filter must be due to biological removal (Graham 1999; Sontheimer *et al.* 1988). This is not always the case, as the adsorption sites on the activated carbon available to DOC are not necessarily the same as those available to target compounds such as algal metabolites. It is also believed that the application of ozone prior to GAC will result in a more effective biofilm on the filter due to the increase in the biodegradability of the oxidised NOM compounds (Huck 1999). Again, this is not necessarily an advantage, as studies have shown that ozonation can result in an increase the biomass on a filter, but the ability of the

Table I Parameters of ozone/GAC pilot plant

Ozone Contactor		GAC Filters		GAC
1 clear PVC column		2 clear PVC columns		Picazine carbon, chemically activated wood-based carbon, produced by PICA Carbon
Diameter	8 cm	Diameter	8 cm	
Height	4.2 m	Height of GAC	1.5 m	
Water flow rate	60 L hr ⁻¹	Water flow rate	25 L hr ⁻¹	
Contact time	15 min	Empty bed contact time	15 min	
Ozone residual	0.3 mg L ⁻¹			
Ozone	Ozonia CFSI, compressed air feed			

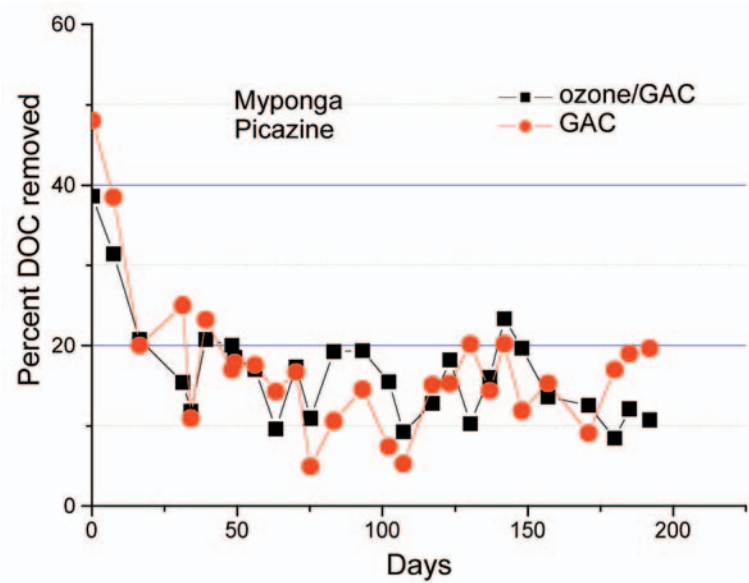


Figure 1 Percent removals of DOC by ozone/ GAC, and GAC alone

biofilm to assimilate a wide range of compounds can be reduced (Moll *et al.* 1999). For example, there is no evidence in the literature that preozonation will increase the ability of a biofilter to degrade MIB or geosmin.

Figure 1 shows removals of DOC through a pilot plant filter run at the Myponga water filtration plant over a period of 200 days. The influent water to the pilot plant was filtered water, sampled prior to chlorination (details of treatment and pilot plant are given in Table 1). One pilot treatment train consisted of ozone followed by GAC and the other was GAC alone. The plateau region of the curves are the same for both treatment trains, within experimental error, and are considered to represent the “exhaustion” of the adsorbent (Sontheimer *et al.* 1988). In this case no enhanced removal of NOM was noted after ozonation. There are several possible reasons for this behaviour:

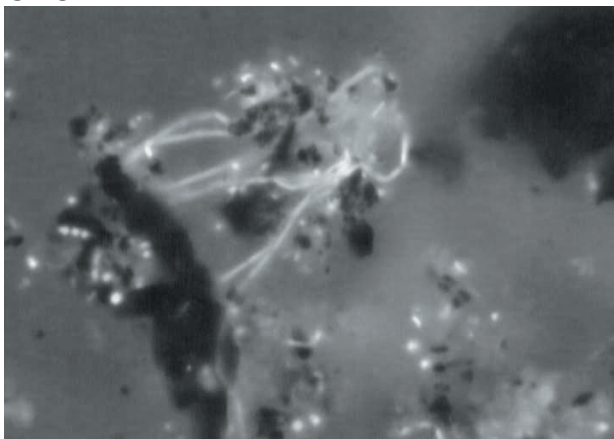
- biodegradation may not be a mechanism of removal of NOM at this stage of the trial,
- ozonation hasn’t increased the biodegradability of this NOM

- the biodegradability of the NOM may have increased while the adsorbability could have decreased due to greater polarity of the oxidised NOM. In this case, if the removal were due to a combination of adsorption and biodegradation, the competing effects may have resulted in little net effect on the DOC removal.

These results suggest that the effect of ozonation on DOC removal is not straight forward, and is dependent on the type of NOM present prior to and after ozonation.

Figures 2 and 3 show that both GAC filters maintained a flourishing biofilm at the conclusion of the pilot trial. Through these qualitative measurements it was not possible to discern a difference between the ozonated, and non-ozonated GAC filter. That is, both were probably functioning as biofilters to some extent.

GAC



Ozone/GAC

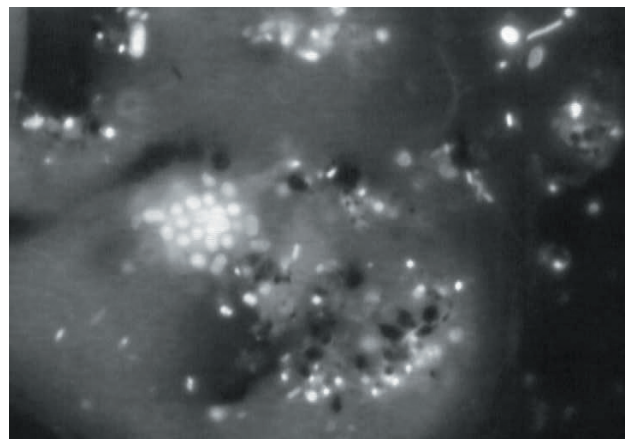
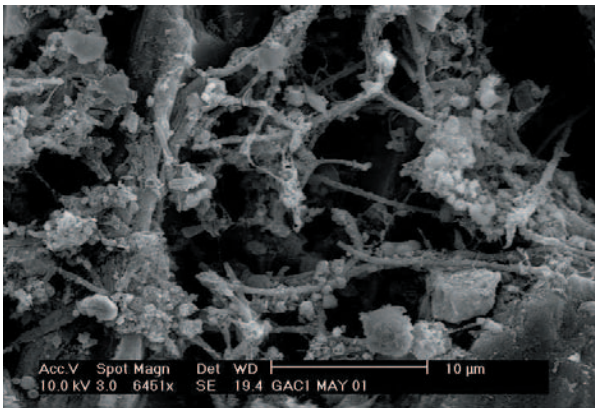
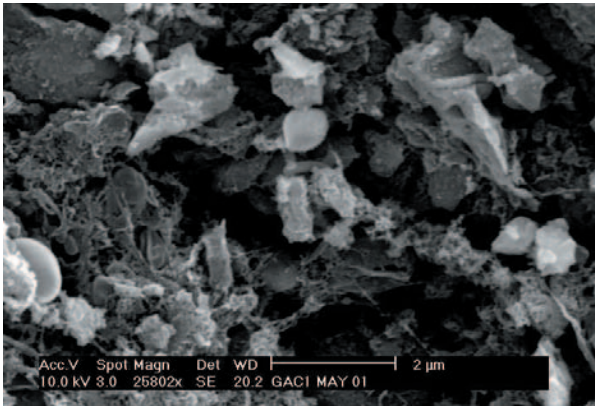


Figure 2 Microorganisms in backwash water of pilot plant GAC filters after 6 months. Photographed using DAPI staining.

GAC



Ozone/GAC

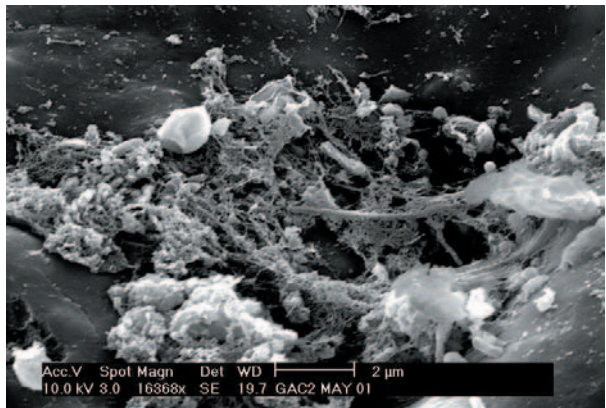
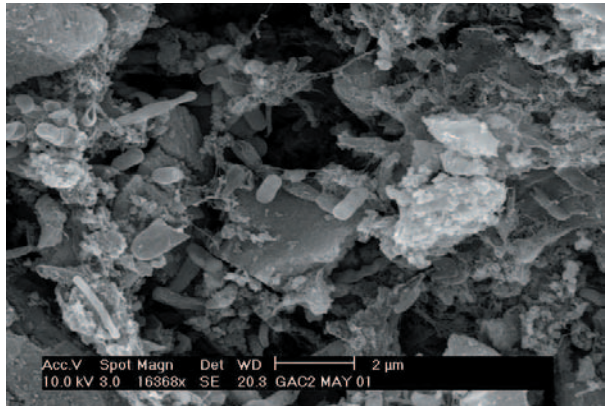


Figure 3 Biofilm on pilot filter GAC after 6 months, photographed using SEM.

MIB and Geosmin

The pilot plant was spiked after 5 months with a mixture of MIB and geosmin at concentrations of approximately 50 ng L⁻¹ each. The taste and odour compounds were removed to below detection by both treatment trains. As this carbon was not expected to remove these compounds effectively (Newcombe *et al.* 1994, 2002) the high removal efficiencies were attributed to biological degradation. At the end of the pilot trial, samples of GAC from the treatment train without ozonation were placed in laboratory-scale columns for further testing. MIB and geosmin were spiked into the influent of the column and

the removal was determined (Figure 4). Also shown are data obtained after sterilising similar carbon samples using three different techniques, including the technique used for the microcystin study, described below. The results show that the high removals of MIB and geosmin cannot be attributed to biological degradation, and are probably a result of adsorption into the micropores of the activated carbon not occupied by the pre-adsorbed NOM. However, it is difficult to exclude the possibility of adsorption of the compounds onto the remaining biofilm, and this mechanism could be contributing to the removal. Further research is required in this area.

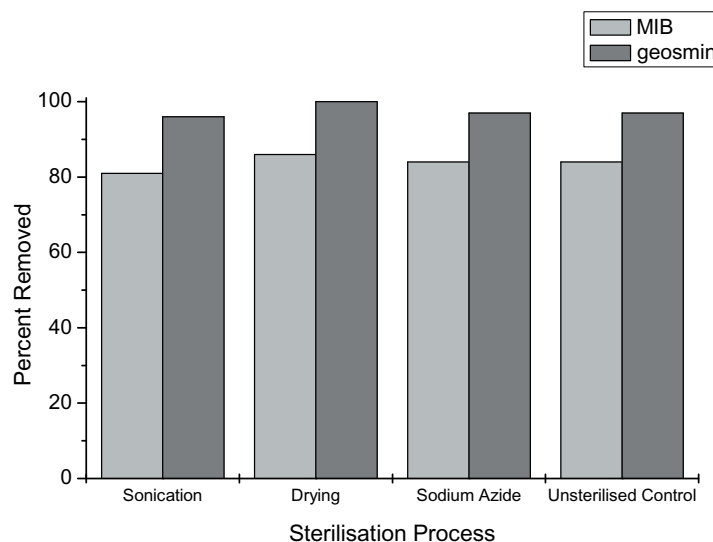


Figure 4. Removal of MIB and geosmin by sterilised and unsterilised GAC.

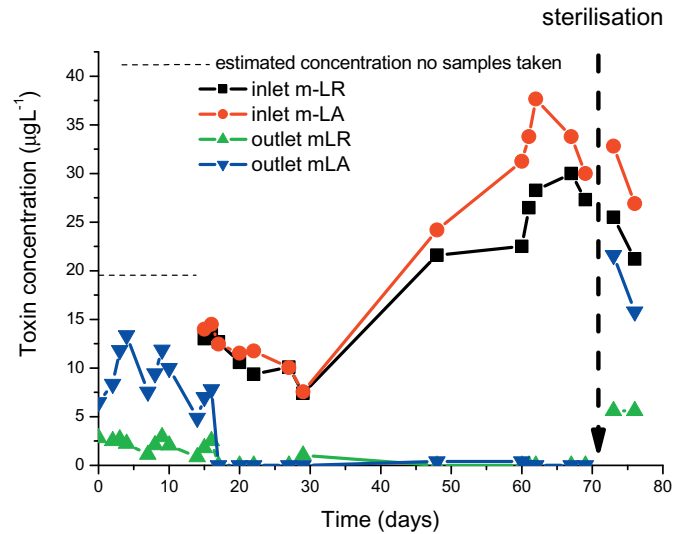


Figure 5 Inlet and outlet microcystin concentration vs. time, lab-scale GAC column.

Microcystin Variants

Microcystin toxins are of higher molecular weight than MIB and geosmin, and adsorb in pores that DOC molecules can also be expected to utilise (Newcombe *et al.* 1994). Therefore, GAC functioning only as an adsorbent allows the toxins to break through into the effluent of the filter after a relatively short time. Figure 5 shows the removal of two of the microcystin variants, microcystin LR (m-LR) and microcystin LA (m-LA) in a laboratory scale column using the same carbon described for the MIB and geosmin study, above. It has been reported previously that m-LA is not as readily removed by activated carbon as m-LR (Newcombe 2002a). Therefore the relatively low removals of m-LA at the beginning of the experiment indicate that the column was functioning in predominantly adsorption mode. After several weeks the outlet concentrations were reduced to below the detection limit of the toxin analysis. This is a strong indication that the biofilm on the carbon had acclimated to the toxins, and was effectively degrading the compounds. Additional evidence for this removal mechanism is shown at the end of the trial, after the carbon was removed and sterilised using the heat treatment used above for MIB and geosmin.

The mechanism was once again adsorption and the removal was much reduced compared with that prior to sterilisation.

Further work has shown that the lag phase before biodegradation begins (days 0-16, Figure 5) can be eliminated by exposing the biofilm to the toxins several times.

Identification of Degrading Microorganisms

Bacteria were removed from the GAC pilot column using vortexing at the two month stage of the pilot trial. The supernatant was decanted into a sterile 30 mL polycarbonate container to ensure that reattachment of the microorganisms did not occur. This resulted in an indigenous bacterial inoculum from the Myponga GAC column. This inoculum was added to sterilised Myponga treated water containing a range of nutrients and m-LR and LA. Details of the process are given elsewhere (Newcombe 2002b). Bacterial numbers in the bioreactor increased initially, then decreased. After 16 days no microcystins remained in the vessel. A sample of water from this bioreactor was added to Myponga treated water containing spiked m-LR and LA, with no added nutrients.

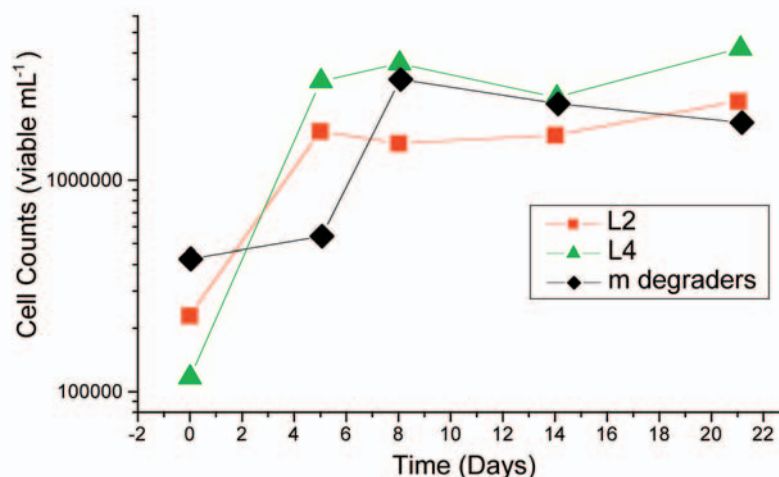


Figure 6. Cell counts of viable bacteria as a function of time in three batch reactors.

This resulted in a bacterial density of approximately 10^5 cfu mL⁻¹. The bioreactor was incubated at 25°C and stirred continuously with a magnetic stirrer for a period of 3 weeks. Samples were taken at day 21 for m-LR and m-LA analysis, which indicated degradation of the toxins to below detection. The bacteria in this sample were enumerated by 0.1 mL spread plates using agar medium, and the colonies formed were used for the identification of bacterial isolates. Four isolates were identified and reinoculated into 2 litre bioreactors as described above, independently and as a mixture. During the same experiment bacteria from a lab-scale GAC column actively degrading microcystins were vortexed from the GAC and inoculated into a separate bioreactor. Figure 6 shows the bacterial numbers analysed by flow cytometry over the experimental period for two of the isolates (L2 and L4) and the bacteria vortexed from the GAC (m-degraders). The other bioreactors showed similar behaviour. The bacterial numbers remained fairly steady, within experimental error. However, degradation of the toxins was only seen in the m-degraders bioreactor. A series of batch degradation experiments undertaken subsequently displayed no degradation of microcystins, although the bacteria were extracted from a laboratory scale GAC column actively degrading m-LR and m-LA.

CONCLUSIONS

The process of biofiltration through GAC, in the presence or absence of pre-ozonation, is not as straightforward as sometimes indicated in the literature.

After a certain period most filtration media will function biologically, providing the surface is suitable for biofilm attachment. Pre-ozonation may increase the biodegradability of the NOM, depending on the character of the NOM; however, the process may also reduce the adsorption of DOC, and the two processes are difficult to distinguish in a porous material such as GAC. This also applies to the removal of MIB and geosmin. These compounds are of low concentration, and very low molecular weight compared with the bulk of the NOM, and in a GAC column there is a large surface area available for adsorption. In the absence of evidence, it should not be assumed that removal of these compounds by an "exhausted" GAC is due to biological processes. In contrast, the microcystins tested are not well removed by physical processes in the exhausted GAC, and the onset of biological degradation through the filter is quite clear.

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- Degradation may be due to some unknown synergistic relationship between different bacteria

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REFERENCES

- Graham NJD (1999) Removal of humic substances by oxidation/biofiltration processes - A review. *Water Science & Technology* **40**(9), 141-148.
- Huck PM (1999) Development of a framework for quantifying the removal of humic substances by biological filtration. *Water Science & Technology* **40**(9), 149-156.
- Jones G and Orr P. (1994) Release and degradation of microcystin following algicide treatment of a *Microcystis Aeruginosa* bloom in a recreational lake, as determined by HPLC and protein phosphatase inhibition assay. *Water Research*, **28**(4), 871-876.
- Moll DM and Summers RS (1999) Assessment of drinking water filter microbial communities using taxonomic and metabolic profiles. *Water Science & Technology* **39**(7), 83-89.
- Newcombe G (2002a) Removal of natural micro-contaminants from drinking water. In: *Encyclopaedia of Colloid and Interface Science*, Marcel Dekker, Inc. New York.
- Newcombe G (2002b) *Removal of Algal Toxins using Ozone and GAC*. AwwaRF report number 90904, Denver, USA.
- Newcombe G, Donati C, Drikas M and Hayes R (1994) Adsorption onto activated carbon: Electrostatic and non-electrostatic interactions. *Water Supply*, **14**, 129.

- Newcombe G, Morrison J, Hepplewhite C and Knappe DRU (2002) Simultaneous adsorption of MIB and NOM onto activated carbon: II Competitive effects. *Carbon* **40**(12) 2147-2156.
- Saadoun I and Elmgdadi F (1998) Degradation of geosmin-like compounds by selected species of gram-positive bacteria. *Letters in Applied Microbiology* **26**(2), 98-100.
- Sontheimer H, Crittenden JC and Summers S Chapter 7, Practical use of activated carbon in water treatment, in "Activated Carbon for Water Treatment." DVGW-Forschungsstelle, Engler-Bunte-Institute, University of Karlsruhe, FRG, 1988.
- Tanaka A, Oritani T, Uehara F, Saito A, Kishita H, Niizeki Y, Yokota H and Fuchigami K (1996) Biodegradation of a musty odour component, 2-methylisoborneol. *Water Research* **30**(3), 759-761.

(Footnotes)

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CRC for Water Quality
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The Cooperative Research Centre (CRC) for Water Quality and Treatment is Australia's national drinking water research centre. An unincorporated joint venture between 30 different organisations from the Australian water industry, major universities, CSIRO, and local and state governments, the CRC combines expertise in water quality and public health.

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