



Mendooran Water Treatment Plant Audit Report

for Warrumbungle Shire Council & NSW Department of Health

4 May 2015



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1 Introduction

City Water Technology (CWT) has been engaged by NSW Health to offer support to numerous utilities in the areas of water treatment process review, assistance with plant optimisation and development of operator procedures. CWT (Bruce Murray and Jacquelyn Osborne) visited Mendooran water treatment plant (WTP) on March 4, 2015 to evaluate the plant and take note of any issues as seen by operators and supervisory staff.

1.1 Overview of Drinking Water Supply System

Mendooran WTP treats and supplies water to consumers in the Mendooran and surrounding communities. Raw water is sourced from the Castlereagh River and a local back up bore (when required), treated at the WTP, and then distributed to the Coolabah 1, 2 and 3 Reservoirs and Standpipe Reservoir. The Mendooran and surrounding communities can receive water from any of these storages, with booster chlorination facilities in place for water from the Coolabah reservoirs. An overview of this system is shown in Figure 1-1.

Mendooran is a conventional WTP combining oxidation, coagulation, flocculation, sedimentation, and filtration. The WTP typically runs for approximately 10 hours per day and averages two starts to maintain water pressure in the reticulation.



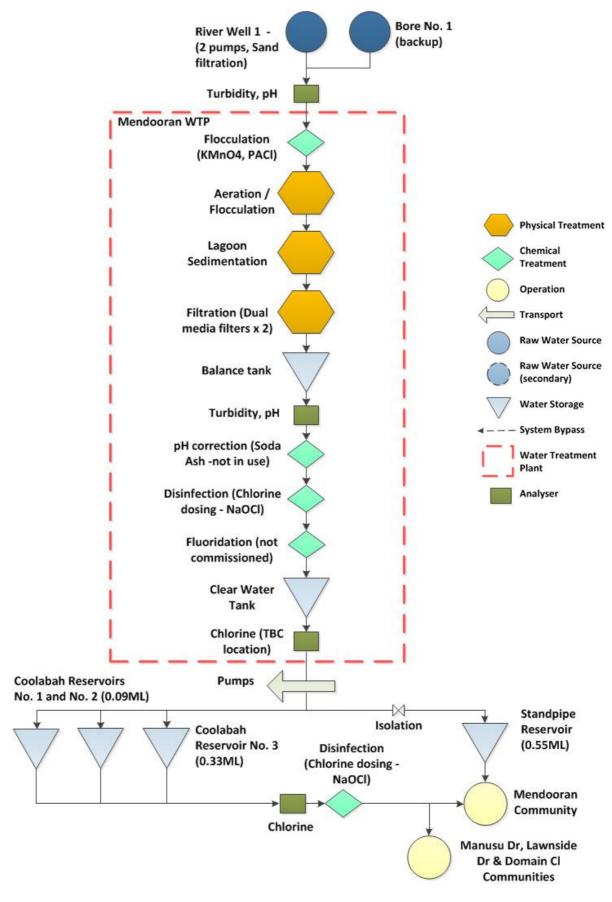


Figure 1-1: Mendooran Water Treatment and Supply System



2 Water Quality Assessment

Parameter	Total Samples	Min	Mean	95%ile	Max	ADWG Value	Comments
Raw Water							
рН	46	7.18	7.51	7.78	7.85		
Settled Water							
рН	45	8.05	8.24	8.33	8.42		
Turbidity (NTU)	4	0.23	0.3	0.41	0.43		
Filtered Water							
рН	9	7.63	7.77	7.9	7.9		
Turbidity (NTU)	46	0.11	0.24	0.38	0.71	<0.2	Target for control of Cryptosporidium and Giardia
Clear Water							
рН	24	7.78	8.12	8.36	8.39	6.5 - 8.5	Aesthetic
Turbidity (NTU)	4	0.11	0.11	0.11	0.12	<1.0	Target at point of disinfection to ensure effectiveness
Chlorine (mg/L)	46	0.4	1.02	1.54	2.89	≤5.0	Health

2.1 Key Points

- ▲ Operational data has only been consistently recorded since December 2014, providing limited data for analysis.
- ▲ Filtered water is often not meeting turbidity requirements to ensure removal of chlorine resistant pathogens *Cryptosporidium* and *Giardia* (<0.2 NTU). The current CCP for filtration at Mendooran WTP requires turbidity to be <1.0 NTU. This should be tightened back to <0.5 NTU and targeting <0.2 NTU to be in line with the current best practice approach to water treatment and pathogen removal, as outlined in the ADWG.</p>



3 Critical Control Points (CCPs)

The CCPs outlined in Table 3-1 were developed by AECOM in conjunction with WSC at a risk assessment workshop as part of the DWMS development project. CWT has analysed the available water quality data with respect to these CCP limits to determine performance and has provided comments for consideration by WSC.

Table 3-1: Mendooran WTP CCPs and Limits

ССР	Hazard and Location	Parameter	Unit	Target Level	Adjustment Limit (AL)	Critical Limit (CL)	Performance	Comments
MDN1: Filtration	All pathogens Filter outlet	Turbidity	NTU	<0.5	>0.8	>1.0	All samples were below the o.8 NTU AL target If the AL is reduced to o.2 NTU in line with ADWG, 79% of samples do not comply	These limits for filtration are quite high when compared to the ADWG recommended targets (see note below)
MDN2: Disinfection	Chlorine sensitive pathogens Leaving Coolabah Reservoir and WTP	Chlorine	mg/L	1.6	<1.2	≤1.0	76% of samples did not comply with AL 54% of samples did not comply with CL	Better control of the disinfection CCP is required
MDN3: Reservoirs	All pathogens and all chemicals	Reservoir integrity	-	No breach	Detection of breach	Evidence of contamination		Not recorded on log sheet
MDN4: Distribution	Chlorine sensitive pathogens and all chemicals	Chlorine	mg/L	>0.5	<0.3	0.1		Not recorded on log sheet

Note: Turbidity targets for the filtration are quite generous considering the current belief that individual filters should be consistently achieving turbidities <0.2 NTU, and never going above 0.5 NTU. While the ADWG states turbidity must be <1.0 NTU for effective disinfection, above 0.2 NTU, removal of chlorine resistant pathogens such as Cryptosporidium and Giardia cannot be assured. CCP limits for this parameter should be adjusted to be in line with best practice for a conventional WTP with filtration.



4 System Details

4.1 Catchment

Mendooran is located in the Central West catchment of New South Wales. Mendooran WTP draws its raw water from the Castlereagh River which runs from Timor Dam (west of Coonabarabran) south through Mendooran before heading West through Gilgandra. Water is drawn off from the river well after filtration through the sand banks by submersible pumps. There are also a number of backup bores that provide water when required, the primary one being adjacent to the pumping site at the river, with a second bore to be brought online near this location shortly.

Concerns have been raised over possible septic contamination of the backup bores and aquifer from irresponsible septic waste disposal via disused bores. An investigation into this was started without yielding conclusive results. Testing should be continued to determine whether these bores are safe to use and if any corrective action by WSC is required.

If possible, these bores should not be used until conclusive results are obtained to guarantee their safety. Additional security measures (e.g. fencing) should be implemented to prevent any further contamination.

Major land uses of this area of the catchment are agricultural, with considerable farming activities, fertiliser application, and possible cattle access to the waterway.

Raw water should be monitored for organic contaminants and excessive nutrient loading that are likely to be introduced through these activities. Additional treatment processes may be required

4.2 Treatment

Mendooran WTP employs a conventional treatment process, having a design capacity of 1 ML/day (12.6 L/s at 22 hr/day operation). Typical flow is generally 6 L/s but can be easily increased if more treated water is required for distribution.

4.2.1 PRE-TREATMENT

Mendooran WTP has significant concentrations of soluble manganese in its raw water (evidenced by the brown staining on the aerator obvious in Figure 4-1), so uses both aeration and chemical oxidation with potassium permanganate to oxidise manganese into its insoluble form so that it can be removed by the conventional process. During commissioning (~5 years ago) soluble manganese levels of up to 2.5 mg/L were recorded in the raw water. More recent manganese data is not readily available as it is not measured at the WTP in the raw water, however total manganese in the treated water leaving the WTP is typically in the range 0.4 - 0.7 mg/L.

The ADWG aesthetic limit for manganese in treated water is 0.1 mg/L with many WTPs preferring to target <0.02 mg/L as above this, consumer complaints of dirty water have been known to increase.

Operators at Mendooran WTP need to begin regular monitoring of the soluble and total manganese



concentration in both the raw and treated waters. Additional laboratory equipment will be required to perform these tests:

- ▲ Nalgene hand pump and vacuum flask with filter; and
- o.2 μm filter papers;

To test for soluble manganese, as opposed to total manganese, the sample needs to first be passed through a 0.2 μ m filter paper to remove any insoluble manganese that may be present in the sample. CWT can provide a procedure for analysing soluble manganese if required. These results can be used to determine the required potassium permanganate dose ratio for sufficient removal of soluble manganese. Typical dosing ratios are a 2 mg/L dose of potassium permanganate for every 1 mg/L of soluble manganese present (2:1 ratio). If organics are present, the dose will need to be increased, anywhere up to approximately 10:1, to account for reactions with the organic contaminants instead of manganese.

Oxidation with potassium permanganate is also affected by pH, with higher pH (>8.5) tending to favour oxidation. Optimal pH and permanganate dose should be determined and regularly verified through jar testing.

Water from the Castlereagh River enters the WTP and flows over the step aerator (Figure 4-1) into the flocculation chamber. Aeration (shown in Figure 4-2) oxidises the soluble manganese so that it precipitates out of the water and can be bound up in the floc with other impurities. The top of the aerator has a distributor pipe (Figure 4-3) for coagulant (ACH) and potassium permanganate (KMnO₄) dosing. Both chemicals are dosed with carrier water into the distributor pipe at the same time. By dosing these chemicals together, each is likely to be reducing the effectiveness of the other (i.e. having a neutralising effect). Blockages of the distributor pipe occasionally occur and may be linked to a potential reaction between the two chemicals.



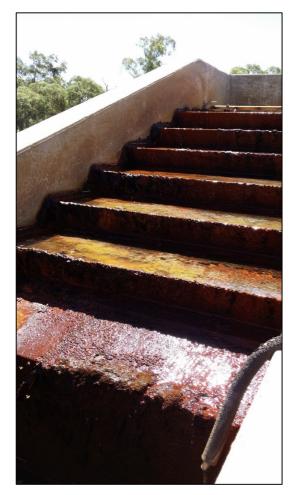


Figure 4-1: Step Aerator (during Down Time)



Figure 4-2: Step Aerator (in Operation)



Figure 4-3: Distributor Pipe at Top of Aerator for KMnO₄ and ACH Dosing

To adequately remove elevated levels of soluble manganese from water sufficient contact time with oxidising chemicals is required. Currently, high levels of potassium permanganate are being dosed with very poor removal efficiency due to virtually no contact time before the addition of ACH. To remove



manganese, it must first be oxidised to its insoluble form then bound up in the floc during coagulation and flocculation and removed by settling. The oxidation process can take at least 3 minutes, with most WTPs opting to target 5 – 10 minutes contact as a minimum to increase removal efficiency.

To provide the necessary contact time the dosing points for $KMnO_4$ and ACH first need to be separated and $KMnO_4$ moved at least 5 minutes upstream of the aerator. This could potentially mean relocating the dosing point to the raw water pump station at the Castlereagh River. Alternatively, CWT recommend that an oxidation tank (~5,000 L) be constructed above the aerator to provide mixing and at least 5 minutes contact time with $KMnO_4$ before gravitating to the top of the aerator for ACH dosing. This will allow time for the oxidised manganese particles to form before addition of ACH so that they can be bound up in the floc. With increased contact time prior to coagulation a lower potassium permanganate dose may be achievable and much more efficient manganese removal can be expected.

4.2.2 COAGULATION AND FLOCCULATION

Coagulation and flocculation at Mendooran WTP is accomplished by ACH dosing at the top of the aerator which mixes with the water as it flows down into the flocculation chamber. The flocculation chamber has concrete baffles, shown in Figure 4-4, which provide hydraulic mixing for improved floc formation.



Figure 4-4: Flocculation Chamber

Coagulation pH is monitored but not controlled, however ACH is an effective coagulant over a wide pH range, approximately pH 6 – 9. The raw and settled water typically have a pH range of \sim 7.3 – 8.3, which is well within the optimum range for effective coagulation.

Significant algal growth was observed in the flocculation chamber (Figure 4-5 and Figure 4-6) and on the aerator surface.





Figure 4-5: Algae in Flocculation Chamber



Figure 4-6: Algae in Flocculation Chamber

Algae can release toxins and taste and odour causing compounds into the water which require extra process steps to remove. At Mendooran WTP there are no additional processes to remove organics and safeguard against organic contamination once it has entered the WTP, so it is important to prevent entry. Algae currently in the flocculation chamber and on the aerator surface should be removed by skimming and application of sodium hypochlorite liquid when required, to avoid any potential release of any toxins or other compounds.

Operators should begin monitoring the concentration of algal cells and nutrient levels (e.g. nitrogen and phosphorus from fertilisers) in the raw water. Additional barriers in the catchment area and improved control over land usage may be required to minimise nutrient loading in the raw water. Powdered activated carbon (PAC) dosing at the WTP may be required if preventive barriers are not sufficient.

4.2.3 SEDIMENTATION

Clarification is performed in one of two sedimentation lagoons. These are rotated on and offline when required so that, when full, they can dry out and the sludge can be removed. Lagoon 2 is currently in use, shown in Figure 4-7. Settled water feeding the filters typically has a turbidity of ~0.3 NTU.





Figure 4-7: Sedimentation Lagoon 2 (In Use)

Extensive algal growth is evident in the lagoons, creating a noticeable scum on the surface (more detailed photos in Figure 4-8 and Figure 4-9). A significant rise in pH (~1 pH unit) has been noted between the incoming raw water and the settled water entering the filters. This is unexpected as there are no chemicals being dosed into the process for pH correction, or that would alter the pH as a consequence, to explain this phenomenon. Therefore, it is quite likely that this anomaly is related to the substantial presence of algae in the system.



Figure 4-8: Algae in Sedimentation Lagoon

Figure 4-9: Algae in Sedimentation Lagoon

There are two likely possibilities which could be causing , or contributing to, this unexpected rise in pH:

- ▲ Consumption of CO₂ by algae for respiration; or
- Release of CO_2 during aeration.

ALGAE RESPIRATION

To grow, algae require light, CO_2 , and nutrients. The aerator, flocculation chamber and sedimentation lagoons are all fully exposed, and given the nature of the land uses in the surrounding catchment area, it is highly likely that nutrients are being introduced into the raw water through cattle and agricultural activities such as spreading fertilisers.

As CO₂ is acidic in water, if it is consumed by the algae during respiration, the pH of the water will rise. Elevated pH is often used as an indicator in raw water storages and catchments that an algal bloom has



occurred. Removing accumulated algae and preventing any further from entering, should result in consistent pH throughout the process if algae is the cause.

AERATION

Aeration could be releasing dissolved CO_2 from the raw water also leading to an increase in pH. Dissolved CO_2 is common in ground water sources (such as bores). Surface water is unlikely to have such a significant CO_2 concentration for this to be the sole cause, however aeration could still be a contributor to the rise in pH. Raw water CO_2 content should be analysed to either verify or discard this possibility.

4.2.4 FILTRATION

Two dual media filters are in operation at Mendooran WTP. These units filter an even split of the incoming settled water from the sedimentation lagoons, typically producing filtered water with a turbidity of ~0.2 NTU. Backwashes are triggered by time (8 hours run time) or headloss (1 metre) set points. Performance of each filter is monitored by a differential pressure (DP) cell for headloss throughout the filter run and single online turbidimeter monitoring combined filtered water turbidity (Figure 4-10).

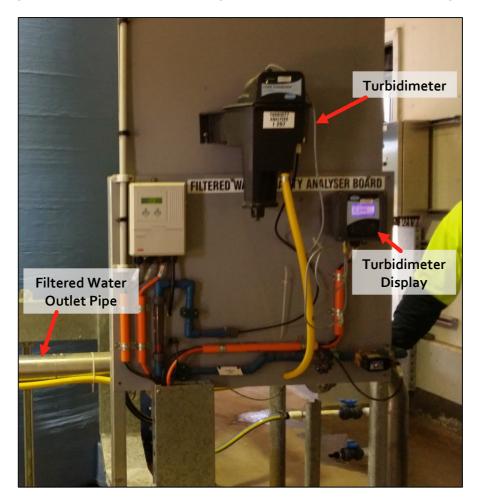


Figure 4-10: Filtered Water Analyser Board

The current ADWG and best practice guides for the operation of drinking water systems recommend online monitoring of all individual filter outlet turbidities to ensure sufficient particle and pathogen removal. If only one filter or the combined water is monitored then this could allow for poor



performance of a filter to go unnoticed if by blending with water from the other filters it was still able to achieve the overall turbidity target.

CWT recommend that WSC relocate the existing turbidimeter to the outlet of Filter 1, and purchase and install a second turbidimeter on the outlet of Filter 2, so that the individual turbidities at the outlet of both filters are being constantly monitored.

Whilst onsite a backwash was observed. All air and water wash rates appeared appropriate and sufficient bed expansion was achieved. It was noted during the air scour the water and media level was well below the bottom of the launder. Upon reviewing the filter design (see Table 4-1) it was noted that the depth of each media layer is lower than recommended for best practice design.

Table 4-1: Filter Media Design

Filter Media Type	Size (mm)	Depth (mm)
Filter Coal	1.3 (Effective Size)	600
Coarse Sand	0.6 – 0.7	300
Fine Garnet	1.2 – 2.4	100
Coarse Garnet	2.4 – 2.8	100

When designing a filter, best practice is for the main filtering layer to have a depth to media size ratio of 1,000, i.e. the filter coal layer should be 1,000 times deeper than the effective size of the media, which for these filters would be 1.3 m.

WSC should consider reassessing the existing filter design and increasing the depth of the media so that it is closer to the best practice size to depth ratio for improved filtration performance.

It was also noticed that inside the filters was stained quite black, likely from soluble manganese entering the filters over time. Figure 4-11 shows significant staining on the internal surfaces of the filter structure and launder.



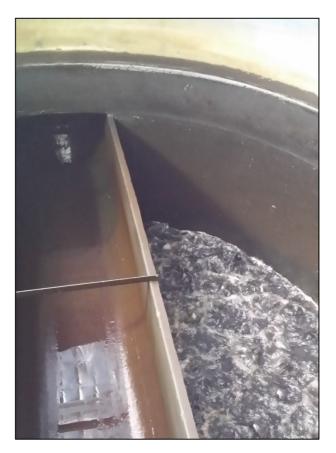


Figure 4-11: Inside Filter 1 during Combined Air and Water Backwash

Wastewater leaving the filters during backwashing (Figure 4-12) was also very discoloured (yellow to dark brown/black) suggesting significant contamination with manganese.





Figure 4-12: Filter 1 during Backwash Showing Manganese Contaminated Wastewater

Given the evidence of manganese in the raw and treated water a multi-barrier approach to removing manganese at Mendooran WTP should be implemented by WSC. In conjunction with optimising potassium permanganate dosing at the head of the treatment works, chlorine dosing into each of the filters should be commenced as a priority.

Filters can be used as an additional barrier for manganese removal by employing manganese oxide (MnO_2) coated filter media. This coated filter media creates additional adsorption sites on the surface of the media that preferentially attract any soluble manganese present in the water. Clean media can be coated with MnO_2 by soaking with $KMnO_4$ and oxidising with continuous chlorine dosing into the filters. Existing media that has been exposed to manganese for an extended period of time (such as those at Mendooran WTP) will likely have a build-up of manganese already on its surface so will not require soaking with $KMnO_4$. Continuous chlorine dosing is required to ensure that the MnO_2 coating stays in its oxidised state and does not reduce back to its soluble form. To reliably maintain the coating, a chlorine residual (nominally 0.1 mg/L) must be achieved in the filtered water at all times.

By combining KMnO₄ dosing and coated filter media almost complete removal of manganese can be achieved. The mentoring notes at the end of this report outline key operational guidelines for effective manganese removal using this approach.

4.2.5 DISINFECTION

Disinfection is achieved by dosing sodium hypochlorite into the inlet to the clear water storage tank. Liquid sodium hypochlorite (NaOCl) is delivered to site at a concentration of 12.5%, where it is then diluted for storage to extend its usable life. It was noted that the chlorine strength does seem to lessen towards the end of the batch, particularly in warmer weather. NaOCl is stored in the chemical storage shed adjacent to the filter and main WTP building.



Chlorine degradation is an important issue as it jeopardises the ability to achieve sufficient disinfection of the treated water. Liquid chlorine is known to lose its potency over time due to dissociation reactions that naturally occur. Heat can increase the rate of reaction, further shortening the expected life of the NaOCI.

To combat these issues at Mendooran WTP, operators firstly need to begin regularly measuring the batch strength of the remaining NaOCI so that adjustments to the dose rate can be made to account for the lower concentration of active chlorine. CWT can provide a procedure for this if needed.

WSC can also consider switching to chlorine gas for disinfection as it does not have the same issues with degradation. Chlorine gas is used at several other WTPs operated by WSC, so changeover to this chemical should be fairly straightforward. Modifications to the storage area and dosing arrangement will likely be required and should be taken into consideration.

While NaOCI is being used at Mendooran WTP, an additional or replacement larger capacity pump will be needed to provide the required doses when using diminished strength chlorine. The chlorine dosing system was initially designed to provide up to 5 mg/L of chlorine at 5% concentration, however maximum pump rate is often reached when using lower strength chlorine without achieving target doses.

The chemical storage shed is quite hot and has little ventilation. WSC should consider insulating this area to lower the internal temperature and in turn extend chlorine life.

Treated water pH is typically in the range ~7.8 – 8.1. For disinfection with chlorine this is quite high and raises concern particularly when combined with issues of unconfirmed chlorine strength, as is the case at Mendooran WTP.

Chlorine is forty times more effective as a disinfectant at pH 7 than at pH 8. Operators at Mendooran should be targeting a lower pH for disinfection, as close to 7 as possible without risking distribution of corrosive water. Resolving pH issues discussed in *Section 4.2.3: Sedimentation* regarding the possible effects of algae and/or CO₂ will assist with this.

4.3 Distribution

From the WTP, water is distributed to one of four reservoirs, totalling ~1 ML of storage – Coolabah reservoirs 1, 2 and 3 and Standpipe Reservoir. Standpipe Reservoir directly supplies the Mendooran community, whereas the Coolabah reservoirs undergo booster chlorination before supplying Manusu Dr, Lawnside Dr and Domain Cl communities and also Mendooran if required.

Mendooran is currently experiencing low mains pressure in the reticulation. WTP operators are trying to minimise these issues by running the WTP more often for shorter periods of time to maintain reservoir levels for greater head to be used as a driving force for distribution.

Maintaining a satisfactory chlorine residual in the reticulation is another issue in Mendooran and the surrounding communities. There is the potential for organics and manganese to be present in the reticulation network arising from insufficient removal at the WTP.

Operators at Mendooran WTP should investigate the chlorine demand of the water to determine the optimum dose required at the outlet of the WTP to provide a suitable residual for all consumers. WSC



should implement a mains flushing program for the reticulation network. This should remove any build-up of organics or manganese that may be consuming free chlorine in the reticulation.

Improved removal of these likely contaminants (potentially: algae, taste and odour causing compounds, and algal toxins) at the WTP will significantly lower the risk of diminished chlorine residual in the reticulation. Implementing a multi-barrier approach to manganese removal as outlined previously can potentially remove virtually all manganese from the treated water. PAC dosing may be needed at the head of the WTP to remove taste and odour compounds and any algal toxins that may be present. Improved catchment management and land use monitoring may be beneficial to lower the risk of algae cells entering the WTP.

4.4 Laboratory

During the site visit, it was noted that the laboratory at Mendooran WTP was lacking in equipment to perform the appropriate routine tests. Below is a list of suggested equipment to conduct general water quality monitoring and jar testing for optimisation of the treatment process.

- ▲ Jar tester 6 jar unit is preferable with square walled plastic/Perspex jars;
- Spectrophotometer more accurate and can measure to a lower range than colorimeters. Appropriate reagents will also be required to perform tests for total and soluble manganese (must be capable of low range measurement), and chlorine residual;
- Turbidimeter both bench top (more accurate) and portable (for field testing) are recommended.
 Will also require calibration standards;
- pH meter pH 4, 7, and 10 buffers will also be required;
- ▲ General lab glassware various glass beakers from 100 mL to 1 L or more with a minimum of six of each size suggested. Measuring cylinders (100 mL, 500 mL, and 1 L), funnels (enough for one per jar during jar testing), and conical flasks (enough for one per jar during jar testing, used for holding funnel with filter paper to simulate filtration);
- 24cm diameter Whatman 1 filter papers (for jar testing);
- ▲ 0.45 and 0.22um syringe filters (for true colour and soluble metals) or alternatively a filter assembly and vacuum pump (either electric or hand pump) with stock of 0.45 and 0.22um filter papers;
- Demineralised/deionised water for rinsing equipment, making up of solutions and preparation of analyses blanks. Can either be bought (through lab suppliers or even at hardware stores or supermarkets) or a filtration system installed (these are costly and tend to require a lot of maintenance);
- Plastic syringes 1 mL, 5 mL, 10 mL for jar test dosing, and 60 mL for extraction of samples;
- Waste disposal containers may be required for some reagents e.g. arsenic used in low range manganese testing; and
- ▲ Latex/nitrile gloves and PPE e.g. safety glasses.

Before purchasing new equipment and reagents a review of the current stock in the lab and recalibration of all instruments should be performed to determine necessary purchases. Additional operator training in how to use these new instruments and when and how to perform the necessary testing may be required.





5 Recommendations

The findings and recommendations from the site visit are summarised below in Table 5-1. Each recommendation is listed in priority order by process step.

Table 5-1: Recommendations for Improvements for Mendooran WTP from Site Audit

Recommendation	Priority
Review Filtration CCP to be in line with ADWG recommendation (<0.2 NTU).	Very High
Continue to investigate sanitary quality and security of back-up bores aquifer.	Very High
Install a second turbidimeter on the outlet of filter 2 and reconfigure the existing turbidimeter to monitor filter 1.	Very High
Monitor raw and treated water soluble and total manganese concentrations and determine optimum potassium permanganate dosing ratio and pH.	Very High
Reconfigure potassium permanganate dosing arrangement to allow 5 minutes contact with raw water prior to addition of ACH.	Very High
Begin dosing chlorine into the filters, targeting a residual of 0.1 mg/L of chlorine in the filtered water outlet.	Very High
Commence regular chlorine batch concentration monitoring.	Very High
Assess the need for additional barriers to be implemented in the catchment area to protect raw water quality.	High
Provide increased pumping capacity for chlorine dosing for disinfection.	High
Investigate the chlorine demand of the treated water in the reticulation to determine optimum chlorine dose at the WTP.	High
Target a lower pH for disinfection.	High
Monitor raw water organics and nutrient loading.	Medium
Remove algae from flocculation chamber and aerator surface.	Medium
Monitor algae cell concentrations in the raw water and sedimentation lagoon.	Medium
Investigate pH increase between the raw and settled water.	Medium
Consider switching to chlorine gas for disinfection.	Medium
Implement a proactive mains flushing program.	Medium
Review the current filter bed depths against the design depths and consider increasing media layers for better size to depth ratios.	Low
Consider insulating the chemical storage shed to lessen chlorine degradation.	Low

6 Next Steps

As Council reviews this document and proceeds with implementation of the above recommendations, CWT will be available for further assistance and any mentoring as required. CWT will continue to liaise with Council to see how the above recommendations have helped improve operations at the plant. If required, CWT can work with WSC to prepare cost estimates for the improvement work suggested above.



7 Mentoring Notes

7.1 Multi-Barrier Manganese Removal

7.1.1 INTRODUCTION

Even at low levels, manganese can cause water colour to range from straw yellow through to black (hence the term 'black water'). It presents aesthetic problems, as consumers may complain of dirty water, stained laundry and plumbing fixtures. Manganese can also contribute to taste and odour problems, particularly if there is microbial growth that concentrates the metals.

Manganese problems are usually intensified by periods of warmer weather. This is primarily because dissolved oxygen concentrations are lower in warmer waters and therefore less natural oxidation of soluble metals occurs.

7.1.2 PRE-TREATMENT OXIDATION

Permanganate has a relatively strong potential for oxidation. Potassium permanganate, KMnO4, is a chemical of crystalline structure which must be made into a solution before dosing. When oxidising manganese, KMnO₄ should be dosed according to a pre-determined ratio of KMnO₄ to dissolved/soluble manganese. Dissolved metals in the water should be closely monitored, and KMnO₄ dosing should be adjusted if the dissolved metal concentration changes. Underdosing will result in incomplete oxidation of metals; overdosing can add dissolved manganese to the water, and any unreacted KMnO₄ may result in pink water.

The theoretical chemical reactions between potassium permanganate and soluble manganese are shown below.

 $3Mn^{2+} + 2KMnO_4 + 2H_2O \rightarrow 5MnO_2 + 2K^+ + 4H^+$

 $3Mn(HCO_3)_2 + 2KMnO_4 \rightarrow 5MnO_2 + 2KHCO_3 + 2H_2O + 4CO_2$

The theoretical stoichiometric amount of KMnO₄ required is 1.92 mg for every 1 mg of soluble manganese (Mn²⁺). Actual dosing ratios are higher than the stoichiometric ratios due to the oxidant demands of natural organic matter (NOM), organically complexed metals, and micro-organisms that may be present in the water. For soluble manganese oxidation, typical potassium permanganate dosing ratios vary from 2 mg to 10 mg of potassium permanganate for every 1 mg of soluble manganese (i.e. ratios of 2:1 to 10:1). For waters where all the dissolved manganese is organically complexed, the ratio may be higher.

Another factor that influences oxidation is the pH of the water. pH values of 8.5 and higher are typically more successful for manganese oxidation by KMnO₄. Jar testing or trials with online adjustments are used to determine optimum permanganate dosing and pH for individual WTPs and raw water sources.

Chemical oxidation (e.g. with KMnO₄) of soluble manganese can be complicated and imprecise, with dosing concentrations reliant upon pre-determined ratios of KMnO₄ to soluble manganese. Underdosing will not be sufficient to oxidise all the manganese present for removal by conventional treatment and overdosing can cause the water to turn pink as well as unnecessarily adding additional manganese to the water which will then require further treatment to remove.



KMnO₄ can be slightly underdosed if this process is coupled with secondary manganese oxidation and removal with subsequent coated media filtration.

7.1.3 PRE-FILTER CHLORINATION AND COATED FILTER MEDIA

Filter media types and properties are selected according to the contaminants in the water. Filter media coated with manganese oxide (MnO_2) is sometimes used to remove manganese from water. It is often used in conjunction with oxidant dosing just prior to the filter, but may also be used on its own. The solid MnO_2 coating catalyses the oxidation of manganese by providing adsorption sites where dissolved manganese attaches. Oxygen or other oxidants (e.g. chlorine) then react with the dissolved manganese at the adsorption site, and the MnO_2 that is formed becomes part of the media coating.

Coated media is a simple and effective way to remove moderate concentrations of manganese from the water stream and can be used independently of any other oxidation and removal processes. Clean filter media is soaked in potassium permanganate which oxidises to leave a solid manganese oxide (MnO_2) coating on the media. The coated media attracts any residual soluble manganese in the water passing through the filters, and adding to the coating.

If the WTP has a long history of manganese in the raw water it may be possible to rely on existing built-up manganese already in the filter media to create the coating. To generate the MnO_2 coating, pre-filter chlorine dosing needs to be commenced. Once a chlorine residual ($\geq 0.1 \text{ mg/L}$) is seen and maintained in the outlet water from the filters, manganese concentrations in the treated water should be much lower.

To maintain the coating there are operational requirements:

- A Maintain a dissolved manganese concentration in the water stream at all times; or
- ▲ Continuously dose chlorine into the filter inlet stream to maintain the MnO₂ in its oxidised state.

Because the process is self-perpetuating under the right conditions, coated media can be a cost effective method of manganese removal. Filter media can be purchased pre-coated (known as 'greensand media'), or coated in situ with appropriate pH and oxidant dosing. Filters should be very clean before coating, or MnO_2 may not properly attach to the media. If the above conditions are not maintained there is the risk that the manganese in the media may reduce back to its soluble form and leave the WTP in the treated water.

The easiest and safest way to ensure the manganese remains in its oxidised state is to constantly dose chlorine into the filter inlet stream. By dosing chlorine there is no risk of adding further manganese into the water. The effectiveness of dosing can be verified by maintaining a constant chlorine residual in the filtered water outlet. It is important that a chemical oxidant (such as chlorine) is <u>continuously</u> dosed into the filter influent stream to ensure that the MnO₂ coating is maintained, <u>even during periods of low or no manganese in the raw water</u> to prevent any existing manganese in the media from reducing and becoming soluble again. To ensure pre-chlorination is effective in maintaining the MnO₂ coating, a chlorine residual should <u>always</u> be seen in the filtered water.



Figure 7-1: Filter Media being Coated with Manganese Oxide

7.1.4 MANGANESE OXIDE FILTER MEDIA COATING PROCEDURE

The following procedure should be followed to coat the filter media with manganese oxide for improved manganese removal.

- 1 Thoroughly backwash filter (possibly 2 or 3 times) to ensure that filter media is clean and free of floc and mudballs. If necessary, caustic wash filter (soak with 1% caustic with air scouring to mix, then backwash out (pH neutralise waste with acid).
- Prepare filter media surface by chlorinating filter media to achieve residual of approximately
 2 mg/L after mixing (air scour) in filter.
- 3 Make-up sufficient volume of 2-3 % potassium permanganate solution (in tank or road tanker) to achieve 0.3-0.4 % potassium permanganate in the volume of filter media plus about 0.5 m above media.
- 4 Drain water in filter down to about 0.5 m above media and add calculated volume of potassium permanganate solution. Air scour to mix.
- 5 Draw potassium permanganate solution through filter media (check for pink water in appropriate sampling point in filtered water line).
- 6 Leave to soak for 24 hours with periodic air scour to mix (2 or 3 times) then backwash filter.
- 7 Check manganese coating using procedure below to confirm 0.2 mg Mn/ g media. Repeat procedure if coating concentration is too low.
- 8 Bring filter on line with pre-filter chlorination. Initially achieve high chlorine residual post filter (> 1 mg/L) then lower to at least 0.2 mg/L free chlorine for ongoing operation once manganese removal is achieved.



7.1.5 MANGANESE OXIDE COATING TESTING PROCEDURE

- 1. Collect media sample & wash gently with deionised water.
- 2. Dry the washed media in a warm oven (30-60 min @ 50°C).
- 3. After cooling take 1 g of the media & place in a 500 mL beaker.
- 4. Add 300 mL of deionised water to the beaker.
- 5. Add 45 mL of concentrated Nitric Acid to the beaker while stirring.
- 6. Add 5 mL of Hydrogen Peroxide to the beaker while stirring.
- 7. Leave for 24 hours.
- 8. Stir the beaker & decant with washing into a 1 L volumetric flask.
- 9. Make the flask up to 1 L with deionised water.
- 10. Test the solution for manganese & report the results as mg of Manganese per litre per gram of media.

Wastewater from the coating process must be handled thoughtfully because of its high contaminant levels, particularly chlorine concentration. The coating process should be conducted at night so that wastewater can be discharged to the drying beds without the chlorine being affected by reactions with UV radiation from sunlight which can lead to odour complaints and changes in water quality. If chlorine is present in the discharge water it should be neutralised with sodium bisulphite (or similar). Subnatant water quality from the drying beds should also be monitored during media coating and wastewater discharge to ensure quality is appropriate for irrigation.

If the filter media is old and there has been a history of manganese issues in the raw water, there may already be sufficient residual manganese in the filter bed to establish a MnO₂ coating simply by implementing pre-filter chlorination, without the need for formalised coating as outlined above.