BALLARAT WATER TREATMENT – THE MANGANESE CHALLENGE

Paper Presented by :

David Both

Author:

David Both, *Operations Manager Ballarat,*

United Water International

67th Annual Water Industry Engineers and Operators' Conference
Sports and Leisure Centre - Wodonga
1 and 2 September, 2004

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THE MANGANESE CHALLENGE

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ABSTRACT

The contractual requirement for manganese (Mn) at the White Swan and Lal Lal WTPs is 0.02mg/L, much lower than the ADWG or WHO guideline values. The drought has lead to highly variable raw water quality and to meet this challenging target a multifaceted strategy to provide rapid responses to changes in raw water quality has been adopted by United Water. These initiatives include monitoring of the reservoir column's water temperatures and behaviour with on-line thermistor chains, depth sampling, assessment of various on-site Mn analysis methods, seeking rapid turnaround times for laboratory analysis and undertaking jar testing to determine appropriate potassium permanganate dose rates. The paper will describe the extent of the challenge, the pros and cons of each facet, and how they have been combined into a strategy that minimises Mn penetration into the Ballarat water supply.

KEY WORDS

Manganese, stratification, thermistors, Ballarat

1.0 INTRODUCTION

1.1 Manganese Formation Theory

Mn is a naturally occurring element in rivers and streams. In water storage reservoirs the decomposition of organic matter in the lower sections of the reservoir may result in anaerobic conditions in which Mn compounds are converted to soluble compounds. Soluble Mn will pass through conventional treatment processes and into the distribution network. When soluble Mn is oxidised to insoluble Mn in the distribution network it forms a dark black particulate substance that can stain clothes, baths, sinks and domestic appliances.

Effective removal of Mn comprises oxidation of the soluble Mn prior to removal of the particulate Mn by coagulation, flocculation and filtration.

1.2 Contract

Ballarat and surrounding townships are supplied with treated water from conventional DAFF plants situated at the White Swan and Lal Lal reservoirs. The plants are operated by United Water International and the treated water quality specification is fixed for the duration of the 25 year contract. Raw water quality risk lies with United Water who is required to meet the treated water specification regardless of the raw water quality. United Water specifies the reservoir offtake to be used but is not responsible for catchment management or reservoir water quality. The Ballarat contract specifies Mn to be measured once a week using a time based composite sampler at the outlet of the treated water storage tank.

1.3 Compliance Limits

Water quality criteria for Mn in water supplies are usually set at the aesthetic guideline value to reduce the risk of staining clothes as mentioned above. Lower concentrations are specified for the Ballarat water supply to reduce the likelihood of Mn oxidising in the distribution network and depositing around fittings such as valves and fireplugs. This can lead to hydraulic blockages and eventually to suspension of lumps of particulate Mn. The guideline values for Mn are listed in table 1.

<u>**Table 1:**</u> ***Manganese Values***

Guideline Values for Mn	mg/L
WHO Health Guideline Value	0.5
ADWG Health Guideline Value	0.5
WHO Usually Acceptable to consumers	0.1
ADWG Aesthetic Guideline value	0.1
Ballarat - Maximum Value	0.05
Ballarat - 95 percent of Samples	0.02

1.4 Design

The White Swan and Lal Lal treatment plants are designed to remove Mn by oxidation with potassium permanganate prior to coagulation, flocculation and filtration. The flow proportional dose is set by manual stroke adjustment and volumetric checks. The maximum design dose rate is 1.7mg/L. Higher dose rates can be achieved by operating 2 pumps in parallel, increasing the batch strength from the design of 5% to the maximum solubility limit of 7.6% (at 25 degrees), or by increasing the pump speed.

1.5 Oxidation Theory

The theoretical reaction of potassium permanganate with manganese is shown below:

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

According to the above equation each mg/L of manganese requires 1.92mg/L of potassium permanganate to convert soluble Mn^{2+} to the solid form MnO_2. Raw water pH as well as chemicals or compounds naturally present in the water will influence the rate of reaction and determine the detention time needed to complete oxidation and formation of a filterable floc.

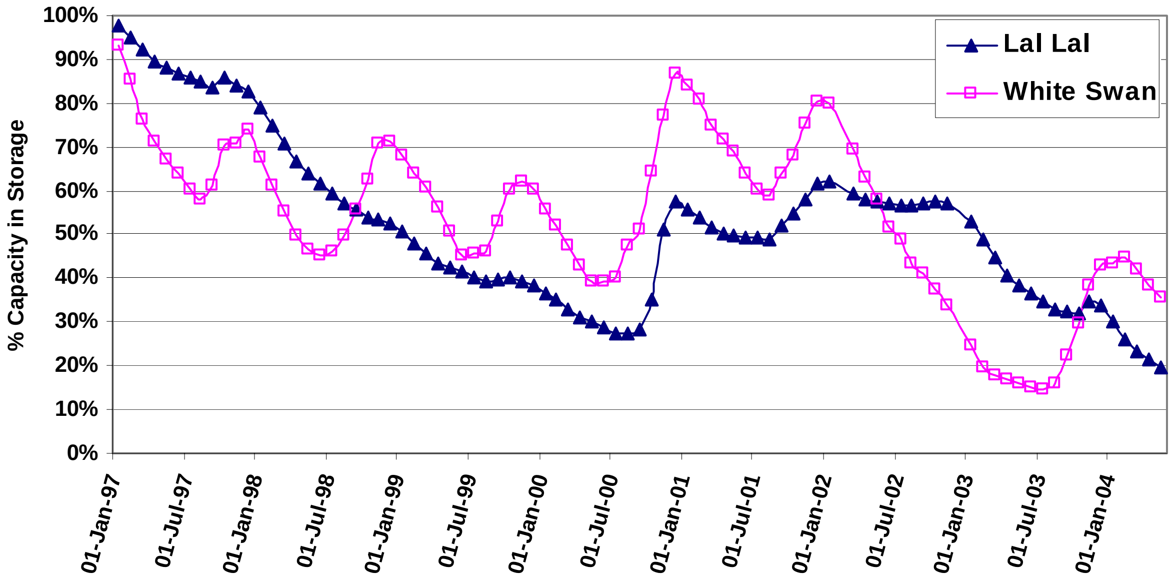
Effective treatment of Mn up to 99% removal efficiency is required to meet to the very low concentrations required under the Ballarat contract and a number of different strategies have been put in place at Lal Lal and White Swan to optimise Mn removal.

2.0 DISCUSSION

2.1 Drought

Ballarat and surrounding areas have received below average rainfall for 8 consecutive years. This has led to diminishing reservoir storage levels as shown in chart 1.

Chart 1: ***Lal Lal and White Swan reservoir storage capacities***

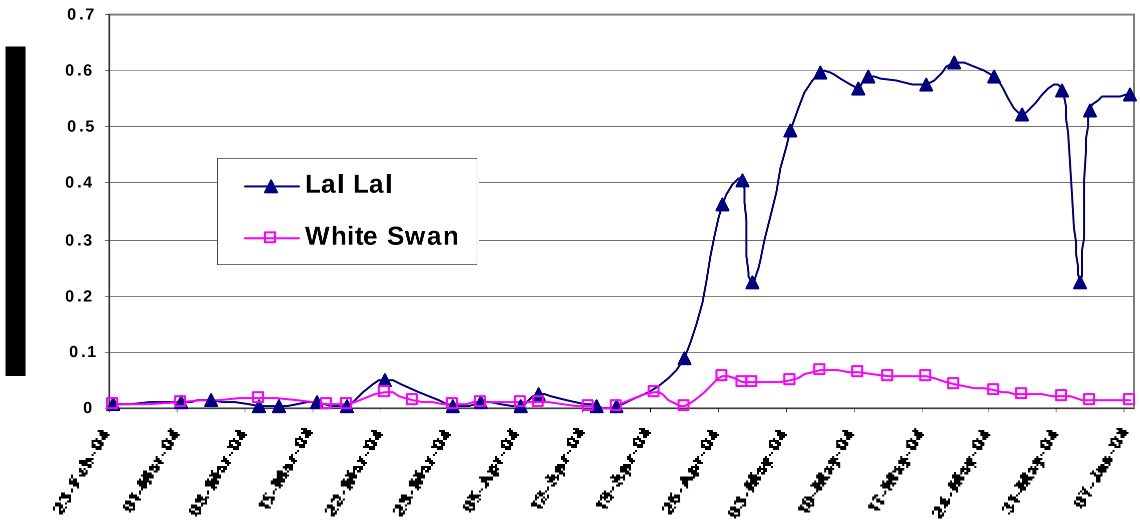


The low reservoir levels currently encountered at White Swan and Lal Lal have caused a number of problems. There are no destratification facilities such as aerators installed in the reservoirs. Consequently both reservoirs stratify over the warmer months with a distinct separation of a layer of warm water near the surface and a colder layer of anaerobic water near the bottom. A rapid change of temperature between the warm and cold layers of water takes place at the thermocline. At the end of summer or during autumn the reservoirs destratify when the warmer layer cools down and suddenly mixes with the colder water below. As the Mn rich cold water mixes with the warmer aerobic water the Mn is oxidised. Soluble Mn is now mixed in the water column and is drawn from the reservoir offtake in use at the time. This soluble Mn will travel through the water treatment plant into the distribution network unless it is oxidised and converted to insoluble Mn before filtration.

At White Swan and Lal Lal there are 4 offtake levels available however the bottom offtake at each reservoir is close to scour level and is not of practical use. Ideally water should be drawn from a level that is below the surface layer subject to algal growth and above the zone lacking oxygen. With low reservoir levels there is currently only one or at best two offtakes available and water cannot be drawn from an ideal level. In addition the low reservoir level increases the proportion of Mn rich anaerobic water in the reservoir which leads to greater concentrations of soluble Mn when the reservoir destratifies.

The variation in raw water soluble Mn at Lal Lal and White Swan in the autumn of 2004 is shown in chart 2. Both reservoirs destratified late in April however the increase in raw water soluble Mn at Lal Lal was an order of magnitude higher than at White Swan. Raw water Mn at White Swan has dissipated since destratification however the Mn concentration at Lal Lal has remained high.

<u>Chart 2:</u> ***Raw water soluble manganese variations***



2.2 Laboratory Analysis

Laboratory analysis using the inductively coupled plasma (ICP) method is the most accurate and reliable method for measuring Mn concentrations. This method provides results to 3 decimal places with a detection limit of 0.005mg/L. This level of accuracy is important particularly when analysing treated water for Mn concentrations below 0.02mg/L.

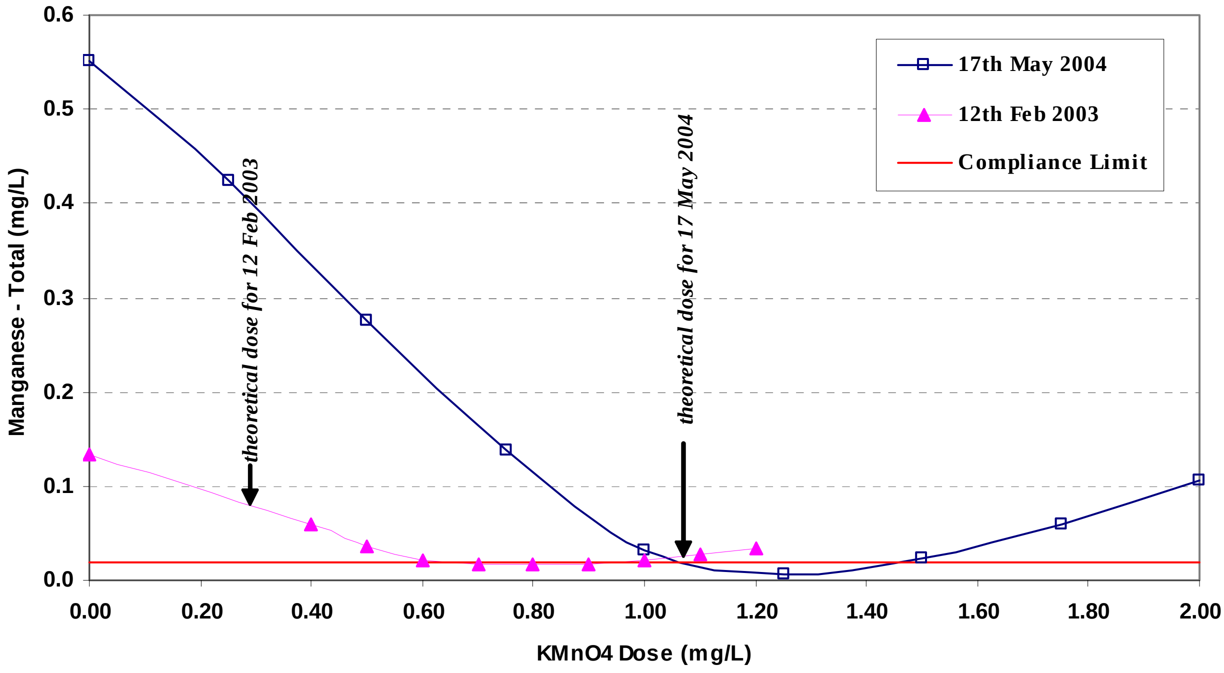
The drawback with using external laboratory ICP analysis to set potassium permanganate dose rates is the delay from sampling to receiving the results particularly from regional centres. A 7 day turnaround time for lab results was typical from the laboratory in Melbourne. Alternative laboratories were contacted regarding turnaround times for Mn analysis. In order to do a same day analysis the sample had to be at the laboratory by 1pm however no transport companies were able to provide a courier service to Melbourne in the middle of the day. Samples are now sent by overnight courier and analysis is carried out by the laboratory that day thereby providing next day results. This enables an accurate potassium permanganate dose to be set based on reliable laboratory results from the previous days sampling.

During high risk periods grab sampling of raw water and treated water is carried out at least twice a week (Monday & Thursday) however with next day results any variation in raw water quality over the weekend period can cause difficulties.

2.3 Jar Tests

Jar tests are useful for assessing Mn removal efficiencies over a range of potassium permanganate doses. However the results are only valid for the water being tested and another set of jar tests is required if the water quality changes. Chart 3 shows that the optimal dose at Lal Lal in May 2004 was close to the theoretical dose however in February 2003 a dose far greater than the theoretical dose was required. Jar tests show the sensitivity of the raw water to the potassium permanganate dose and demonstrate the effect of under and overdosing.

Chart 3: ***Lal Lal Jar Tests***



Jar tests can be carried out on water taken from below the current offtake. This provides information as to the likely dose rates required when the raw water changes and when used in conjunction with thermistor chain data or manual depth measurements can assist in setting optimal dose rates during reservoir destratification.

2.4 Thermistor Chains

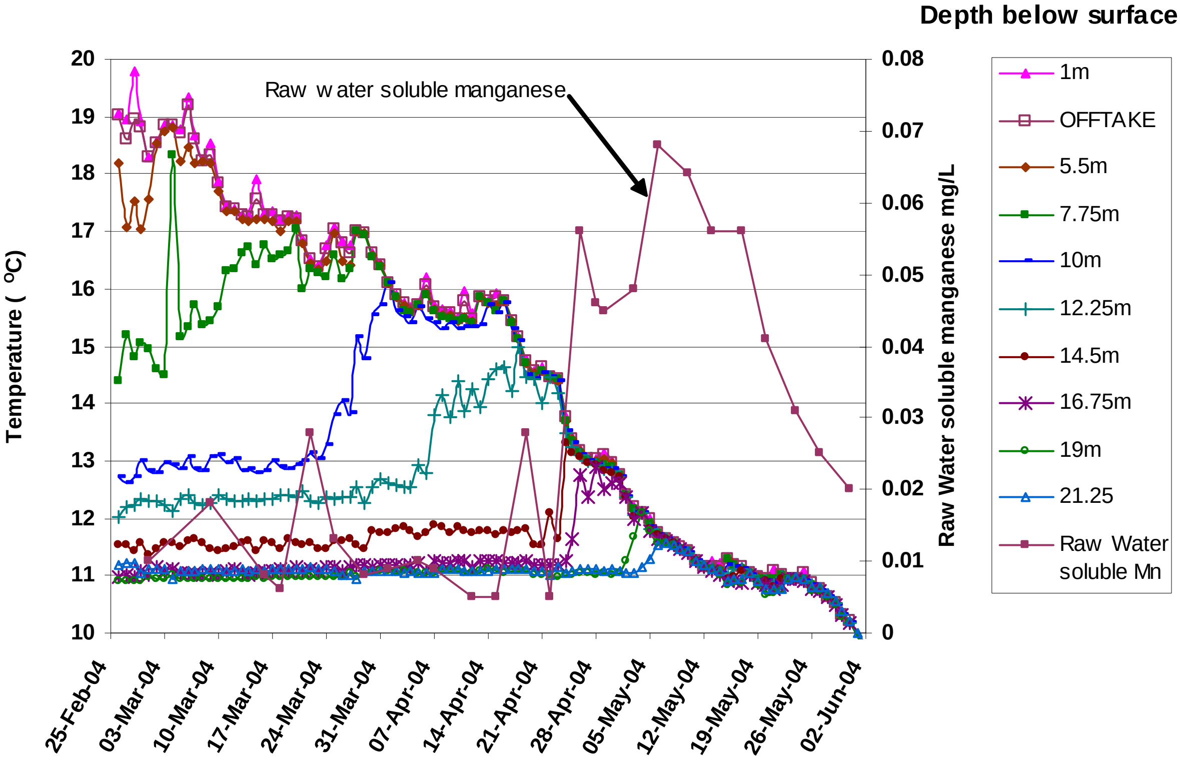
It was evident from previous large and sudden variations in Mn concentrations in the raw water that a better understanding of the conditions in the reservoir was required to enable a more rapid response to changes in raw water quality. Regular reservoir D.O. and temperature data was collected by depth sampling from a boat however experience has shown that daily monitoring is required during autumn each year.

Thermistor chains have therefore been installed in both reservoirs. These chains comprise temperature sensors at 2.25m intervals hung from the reservoir offtake tower. A data logger in the tower records the temperature information. This data is downloaded via a modem using the CDMA network. This is initiated manually from a PC in the plant control room and is done daily during high risk periods.

This real time information can be used to trigger increased sampling and analysis, jar tests or on-site lab analysis. It is important to note that the data needs to be used in conjunction with other sources of information to optimise the treatment process. The thermistors are only measuring temperature and give an indication of changing conditions. Analysis of depth samples from below the thermocline before destratification will assist in predicting Mn changes. The raw water Mn concentrations will vary depending on the dilution factor, the mixing characteristics of the reservoir and the depth of the offtake.

Chart 4 shows the White Swan reservoir destratifying in autumn 2004 and the associated change in the Mn concentration at the offtake near the surface. The temperature changes at 14.5m depth and 19m depth corresponded to rapid increases in raw water soluble Mn.

Chart 4: ***White Swan Thermistor Chain & Manganese***



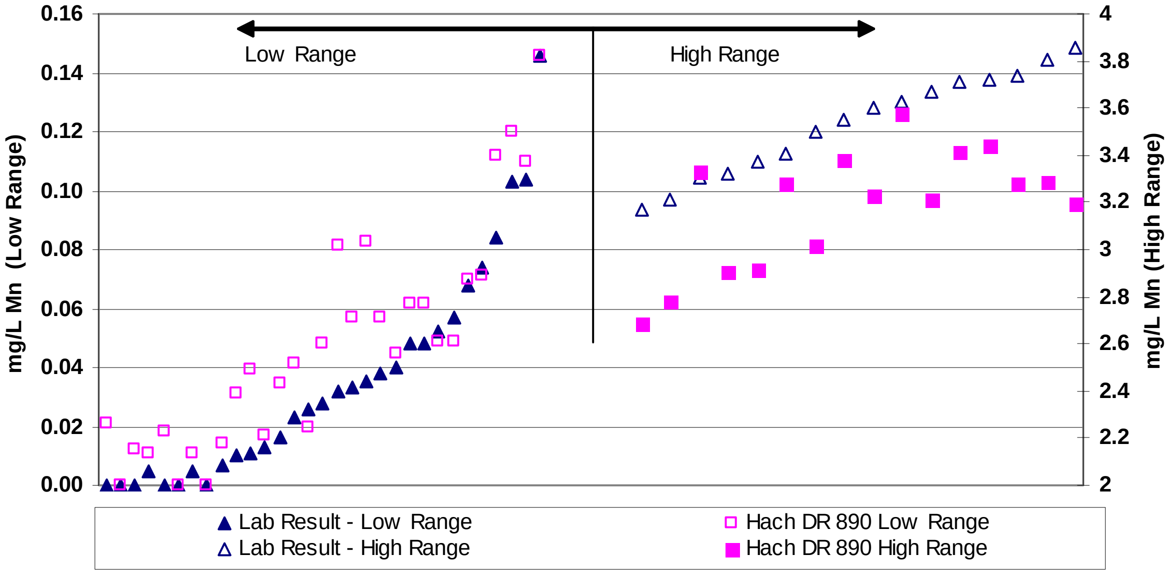
2.5 On Site Analysis

Rapid feedback on raw and treated water Mn concentrations during high risk periods is required. Assessment of two on-site analysis methods is being carried out. Both methods are colourimetric methods with the colour or light absorbance of a prepared sample measured and compared against 'standard' readings to determine the concentration of Mn. These colourimetric methods are not as accurate as the laboratory ICP method due to interferences in the reactions and the natural absorbance of the water which changes from season to season largely depending on the organic content of the water.

The Hach PAN method uses an ascorbic acid reagent to reduce all oxidised forms of Mn to Mn^{2+}. An alkaline-cyanide reagent is added to mask any potential interference. PAN indicator is then added to combine with the Mn^{2+} to form an orange complex. A colourimeter reads the colour of the orange complex at 560nm. A trial of the PAN method with a Hach DR 890 has been carried out. Samples of raw water were spiked with different doses of potassium permanganate to provide a high range Mn concentration above 2.5mg/L and a low range of Mn below 0.1mg/L. Results show the Hach PAN test had a reasonable correlation with the lab results for both the high range and low range. Results are presented in chart 5.

The Hach PAN method provides instant feedback on Mn concentrations however safety and environmental issues with the cyanide based reagent used for the test must be addressed. There is potential for cyanide gas to be produced if the cyanide reagent is mixed with acid. Safe and environmentally sound chemical handling and waste disposal practices should be developed including training of all operations personnel.

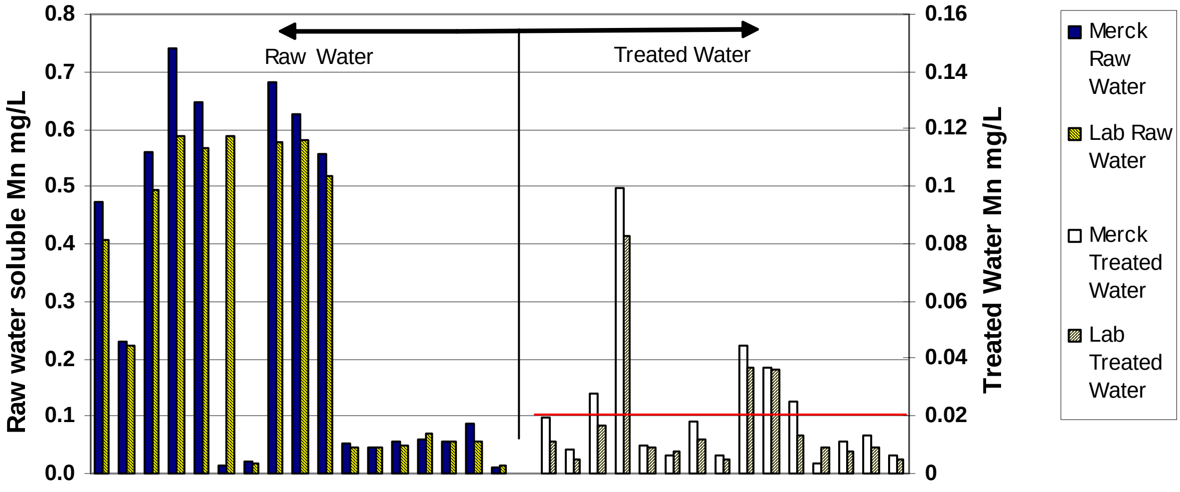
Chart 5: ***Hach PAN Method v Lab Results***



An alternative colourimetric method is the Merck Spectroquant method which does not require a cyanide based reagent. With this method an alkaline masking solution is added to the sample followed by addition of formaldoxime. The Mn reacts with the formaldoxime and a red-brown colour complex is formed. Complexes of accompanying metals formed despite masking are selectively destroyed by a reducing Titriplex solution. The light absorbance of the solution at 445nm is converted to a Mn concentration by a standard conversion factor.

Merck tests were carried out on-site with duplicate samples sent to the laboratory for ICP analysis during the destratification of Lal Lal and White Swan reservoirs in autumn 2004. The method used at Ballarat to negate the influence of background organic colour was to take the difference in UV absorbance of the solution after addition of reagents and the UV absorbance of a 'blank'. Results show a reasonable correlation with lab results for raw water with one distinct outlying result. Results of the Merck tests at White Swan and Lal Lal are shown on Chart 6.

Chart 6: ***Merck Method v Lab Tests***



2.6 On-line Measurement

An alternative to the on-site lab tests are on-line analysers. These units use a colourimetric method and the accuracy and reliability needs to be confirmed over a range of waters for a particular site. Units are approximately $20,000 each with $2,000 per year reagent costs plus maintenance time. No evaluation of these units has been undertaken.

3.0 CONCLUSIONS

Experience gained over 3 years of extreme water quality conditions in the White Swan and Lal Lal reservoirs has demonstrated that multiple sources of information are required to treat Mn to 0.02mg/L. The following strategies are recommended in order of importance.

Establish rapid turnaround times for laboratory results. This enables accurate dose rates to be set however the lack of results over weekends can pose a problem if the raw water quality changes. The costs of analysis also increases as laboratories charge a premium for the increased level of service.

Obtain on-line measurement of temperatures in the reservoir to enable an understanding of reservoir conditions and the potential for changes to raw water quality. Thermistor chains provide real time data on reservoir temperatures and enable high risk periods to be identified. This enables sampling and/or on-site testing frequencies to be increased. However temperature measurements alone do not provide sufficient information on Mn concentrations to accurately set dose rates and depth sampling is required to support the temperature data.

Carry out on-site laboratory tests to get instant feedback on Mn concentrations. Direct comparison with lab results should be undertaken to establish the accuracy of the method used. It is questionable whether on-site colourimetric tests alone can achieve 0.02mg/L with fluctuating raw water Mn concentrations however on-site testing provides valuable information between lab sample results that will assist with dose adjustments. Establishment of procedures for safe storage and disposal of reagents and training of operators is essential.

Carry out jar tests over a wide range of potassium permanganate doses to determine the effect of under or overdosing. Sampling and jar testing from below the thermocline will enable dose rates for worst case scenarios to be established to ensure dosing facilities are adequate.

Install flow meters on the potassium permanganate dosing lines to enable a more accurate and reliable dose to be achieved.

4.0 ACKNOWLEDGMENT

The author would like to acknowledge the valuable input provided by United Water laboratory specialists and operations staff in particular Michael Goulding, Peter Frost, Troy Peterken, Peter Quinlivan and Michael O'Brien.