# MANGANESE REMOVAL USING CHLORINE OXIDATION AND POWDERED ACTIVATED CARBON

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# MANGANESE REMOVAL USING CHLORINE OXIDATION AND POWDERED ACTIVATED CARBON.

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**ABSTRACT**

Draining of Lake Mulwala in May/June 2002 and persistent low rainfall in Springhurst caused raw water quality for the Yarrawonga and Springhurst water supplies to be adversely affected. Lowering water levels in both dams lead to elevated concentrations of Manganese (Mn) entering the treatment plants and reticulation systems. Several methods of Mn removal reported in literature were tested and it was found that oxidation of the Mn using Sodium Hypochlorite with contact times available in the plants and the addition of Powdered Activated Carbon during the flocculation stage achieved optimal removal of the Mn ($P=2.75\times10^{-5}$).

Systems were put in place utilising these findings, which have proven to consistently reduce raw water Mn concentrations in excess 0.42mg/L at Yarrawonga and up to 1.2mg/L at Springhurst to levels well below the guideline value of 0.1mg/L. Particle counting was also found to be a sensitive and effective monitoring tool for indicating Mn breakthrough due to system failures at Springhurst.

## 1.0 INTRODUCTION

In early June 2002 the North East Water (NEW) Yarrawonga Water Treatment Plant (WTP), located on the banks of Lake Mulwala experienced treatment difficulties due to changing raw water quality. Operating staff noticed chlorine residuals were becoming difficult to maintain despite the apparent cleanliness of the filtered water prior to chlorine addition. This lead the treatment plant operators to test for the chemicals Iron (Fe) and Manganese (Mn) in the raw at treated water supplies in an effort to find an answer. It was found that Mn levels up to three times the guideline level of 0.1 mg/L were entering the reticulation system post treatment and that the raw water levels were between 0.37 and 0.42 mg/L Mn. Not long after, several customer complaints regarding dirty water and staining of washing were lodged and a method of removal was under investigation.

These parameters are not tested on a routine basis at the plant as it usually draws water from the surface waters of Lake Mulwala and has had no history of high Mn in the raw water. At the time of the incident the lake was drained for routine (once every ten years) maintenance of the dam wall, leaving available for water only the slow moving Murray River (reduced to minimal winter flows) and bare mud flats usually inundated with water. This led to the significant changes in raw water quality and treatment plant performance that required immediate attention.

Several previously reported methods to remove the Mn were trailed in laboratory jar tests and a solution involving the use of oxidation via pre-dosing chlorine and Powdered Activated Carbon addition during the flocculation stage was implemented.

Following this event, no inflow to the Springhurst reservoir for an extended period led to the slow draining of the Springhurst Reservoir. Again elevated Manganese concentrations were observed and a significant 'black water' event followed. The same method developed during the Yarrawonga incident was employed with success and the removal of Mn monitored via a particle counter.

The following report outlines results obtained from Yarrawonga laboratory testing, the performance of the recommended method of Mn removal through the treatment plant, costs associated with operating the methods on a commercial scale and the use of particle counting to monitor treated water manganese concentrations at Springhurst.

## 2.0 THEORY - BACKGROUND

Why did the water raw quality at Yarrawonga and Springhurst change the way it did? The elements known as Iron (Fe) and Manganese (Mn) are often found naturally in surface waters used for drinking supplies, and are essential elements for healthy life. When dissolved in water Mn and Fe are present in both soluble and insoluble forms. When Mn and Fe are present in a water body they react with oxygen (and other oxidants) to become insoluble in water (i.e. they become solids), when a river course is dammed and water movement (turbulence) is reduced, these solids settle from the still water eventually being deposited on the bottom becoming part of the sediments. The oxidation of Mn forms a very dark if not black stain in the water which can then badly stain clothes and other items around the house.

At most times this 'sinking' of Mn and Fe to the bottom of lakes, does not effect a water treatment plant as these facilities usually draw their water from the upper region of the water column and many can even vary the depth of their water off-take to avoid both anaerobic (oxygen deprived) lower waters contaminated with metals such as Iron and Manganese or in summer months, avoid surface waters with high exposure to sunlight which may experience algae blooms.

When Lake Mulwala was drained NEW had to extend their off-take pipes and commission a new floating pontoon for the raw water pumps in order to compensate for the increased distance required to reach and pump the water from the exposed Murray River. It was not foreseen that Mn and Fe concentrations would increase the way they did, as there had never been an incident related to high concentrations reported before. At Springhurst, high concentrations of Iron had been evident for some time and a removal system utilising aeration and pH elevation for oxidation was in place. This system proved to be insufficient for removal of the Mn concentrations in the raw water. It was approximately one week after the lake had been drained to completion that the elevated Mn concentrations were reported, this was caused by the settling of Mn and Fe to the bottom of the lake over a long time period, via the oxidation process described above.

The problem becomes further compounded by the treatment process itself, where the oxidant, Chlorine is added late in the process for disinfection causes remaining Mn to be precipitated from solution in the clear water storage and reticulation system. To further add to this, any un-oxidised Mn still in the system can be oxidised by detergents used in the home (clothes washing) which can lead to staining of clothes, sinks and tubs.

In order to remove Mn from a water supply general theory to date involve the complete oxidation of the compound either by aeration or using chemicals such as Chlorine, Potassium Permanganate, or Hydrogen Peroxide, followed by flocculation and coagulation of the oxidised solids liberated. These processes are also known to be improved by raising the pH of the water to greater than 8.5, which in itself aids the oxidation process. Several tests were performed at Yarrawonga using chemicals that were readily available (Sodium Hypochlorite) and able to be put in place without any major risk to the staff, consumers or environment.
All tests were performed simulating detention times available in the treatment plant to determine the best option for removal that could be quickly incorporated into the system as it stood.

## 3.0 RESULTS AND DISCUSSION

### 3.1 Yarrawonga

Table 1 outlines the conditions under which jar tests were performed based on calculation of detention times throughout the treatment plant.

**Table 1:** ***Flocculation Parameters used Throughout Laboratory Trials.***

| Pre-dose Chlorine | Rapid Mix | 50 RPM Mix | 10-15 Rpm Mix | 5-10 RPM Mix | Settling Time |
|---|---|---|---|---|---|
| 27 min contact | 30 Seconds | 6 minutes | 10.5 minutes | 19.5 minutes | 45 minutes |

Optimal dose rates for Soda Ash and Polyaluminium chlorohydrate were determined to be 15mg/L soda Ash and 5 mg/L MegaPAC. These dose rates returned a flocculated water of pH 7.3-7.5 with a solid B-C sized flocc. Throughout the three days of lab testing further optimisation of the MegaPAC dose was required and a dose rate of 5.7 mg/L was deemed optimal.

Sodium Hypochlorite was dosed to several samples, mixed and allowed to stand for 27 minutes contact time and residual Free Cl was measured and recorded. Soda Ash and MegaPAC were then added at the pre-determined optimal doses. Results of jar tests performed can be seen in Figure 4.1. It can be seen that a significant relationship exists between chlorine residual concentration and filtered water manganese concentrations (Line of best fit, $R^2$ = 0.9391), however no results were found to be below the guideline limit even with a free chlorine residual of 2.25mg/L. This method was deemed unsuitable for the practical application due to the high residual chlorine levels after settling. It was decided that further tests would be carried out using Hydrogen Peroxide and Powdered Activated Carbon.

**Figure 1:** ***Residual Manganese vs. Chlorine Residual from jar tests with and without Powder Activated Carbon Addition***

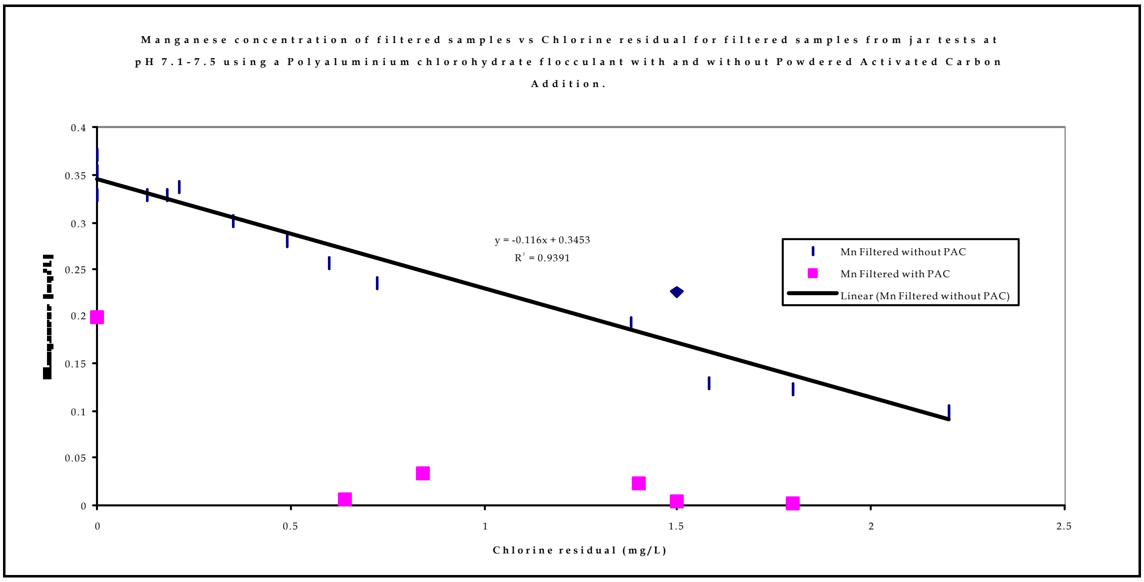



Figure 1 also shows a comparison of results for jar tests where Powdered Activated Carbon was added. These results show a difference in Mn removal between those which had PAC added and those that didn't. Samples where PAC was added showed much lower Mn residuals than those that did not.

The results summarised in Figure 1 were analysed for statistical significance via a 'single factor' (or 'one way') analysis of variance (ANOVA) to determine the significance of the differences observed in the two treatments. A P (probability) value of $2.75 \times 10^{-5}$ was obtained indicating a significant difference in results obtained from the two treatments (see Table 2).

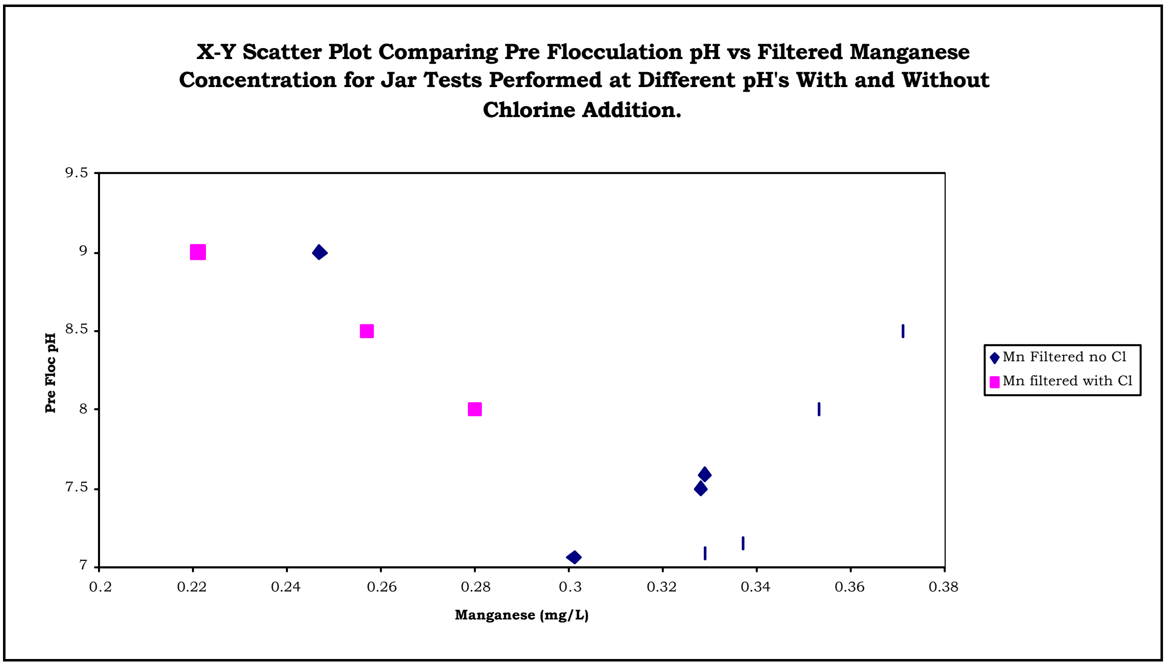
**Table 2:** ***Analysis of variance table comparing samples dosed with Powdered Activated Carbon with those not dosed with PAC.***

| ANOVA |
|---|

| Source of Variation | SS | Df | MS | F | P-value | F crit |
|---|---|---|---|---|---|---|
| Between Groups | 0.21056 | 1 | 0.21056 | 31.02586 | 2.75E-05 | 4.413863 |
| Within Groups | 0.122159 | 18 | 0.006787 | | | |
| Total | 0.332719 | 19 | | | | |

Results obtained from jar tests that raised pH prior to flocculation did not indicate effective removal of manganese, nor was the trend observed significant (Figure 4.2). In samples where chlorine was added also, an improvement in Mn removal with raised pH was observed however all residual Mn concentrations were above the 0.1mg/L guideline limit.

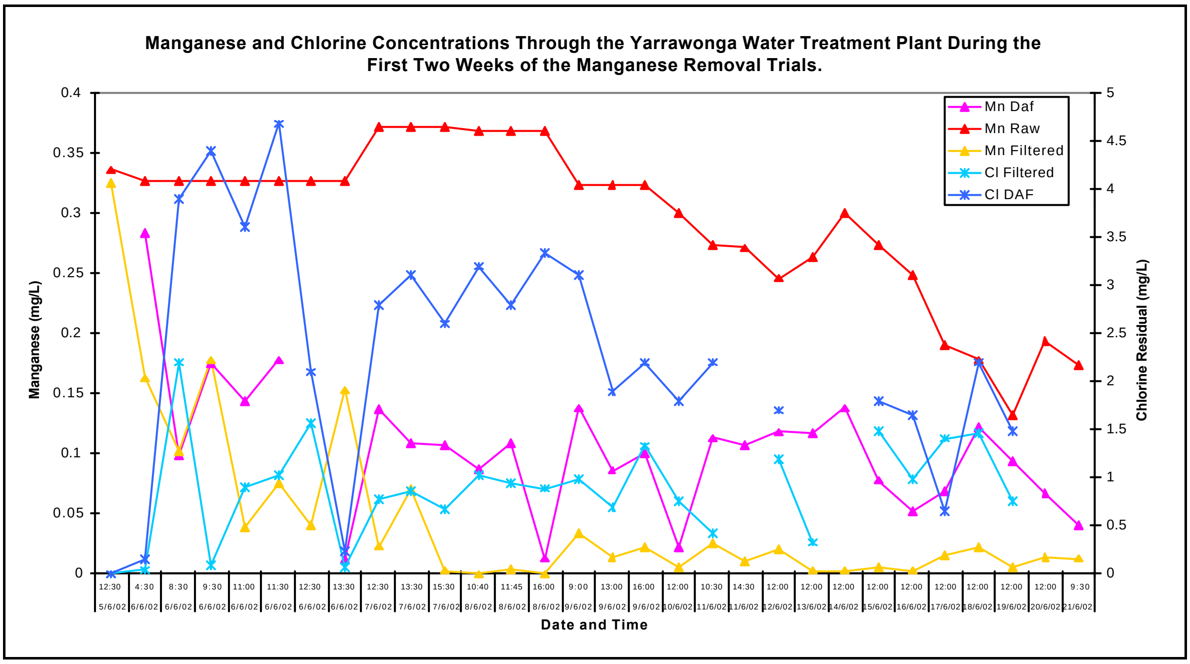
**Figure 2:** ***Manganese residual concentrations V's Pre-Flocculation pH for samples with and without chlorine addition***




From results obtained Mn removal via pre-dosing Sodium Hypochlorite followed by Powder Activated Carbon addition was put into place utilising materials the Authority had available at other sites. Close monitoring of the process over the following two weeks showed a gradual decrease in treated water manganese concentrations over the first day of operation followed by consistent readings well below the guideline value (Figure 3).

Treated water manganese concentrations since two days after the installation of the system have averaged 0.014mg/L Mn, ranging from 0.000 to 0.034 mg/L Mn.

**Figure 3:** ***Manganese residuals throughout the Yarrawonga Water Treatment Plant (6/6/02 – 21/6/02).***




It can also be seen in Figure 3 that the Manganese concentration in the raw water began to decline on the 15th June reaching 0.17mg/L Mn on the 21st June. This trend was caused by rainfall upstream in the catchment that assisted in flushing the manganese from the raw water supply. The upper catchment rainfall event also increased raw water turbidity as can be seen in Figures 4 and 5 reaching a maximum turbidity of 68.1 NTU. Alterations to all chemical doses were required in order to maintain adequate flocculation and effective Mn removal.

**Figure 4:** ***Turbidity - Raw, settled and filtered water samples from Yarrawonga WTP.***

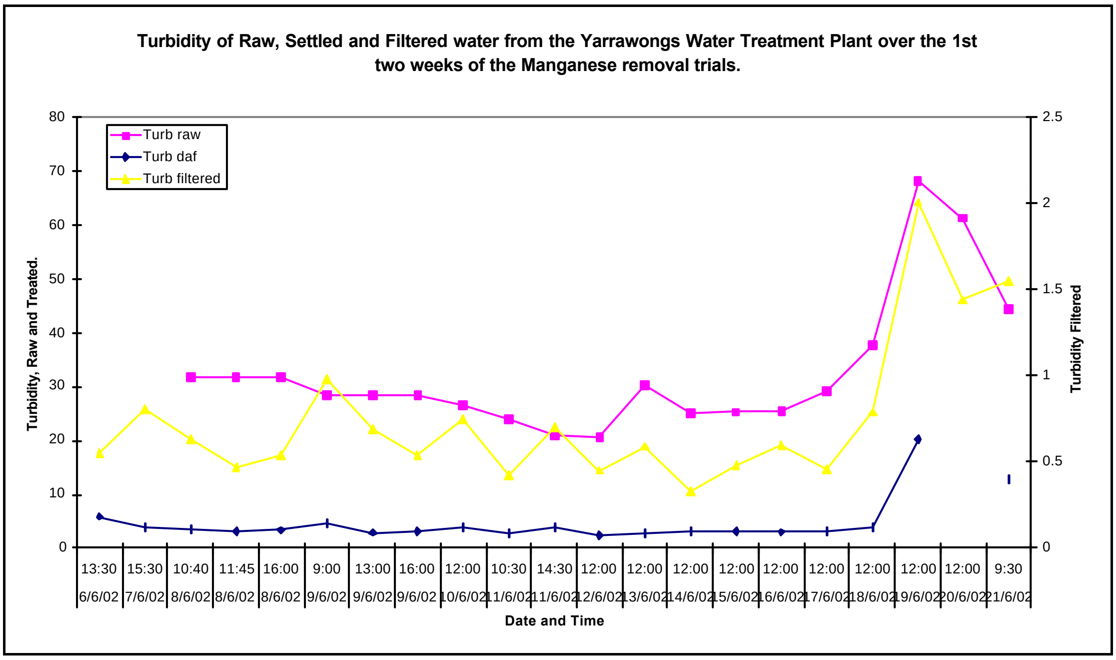
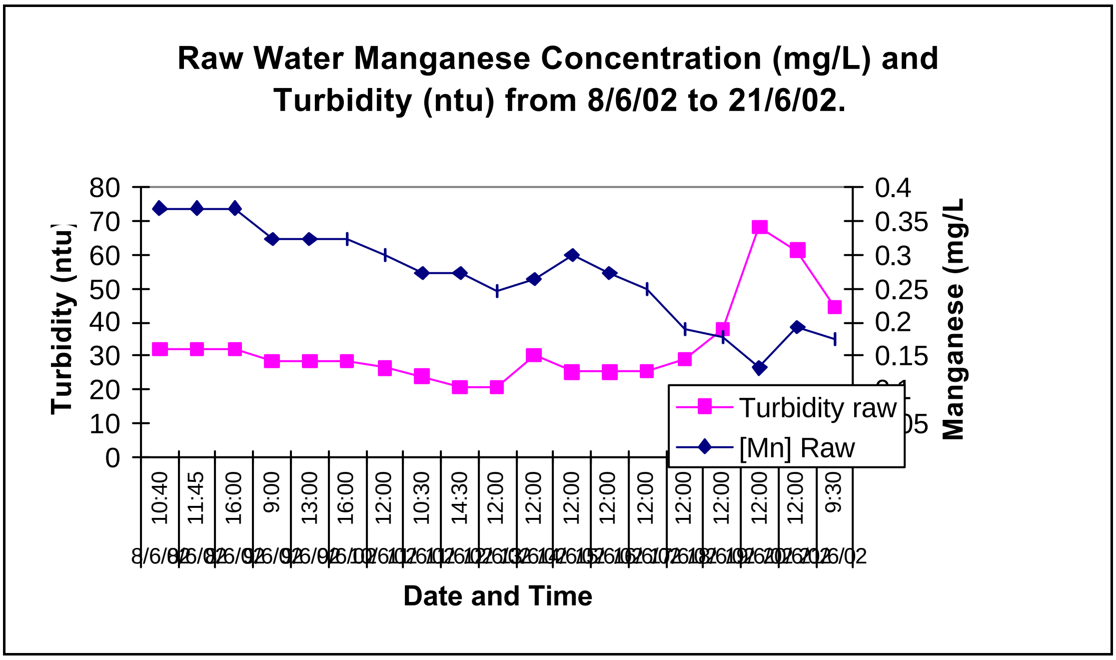



**Figure 5:** ***Raw water Turbidity and Manganese concentrations at the Yarrawonga Water Treatment plant from 8/6/02 to 21/6/02.***




## 3.2 Springhurst Particle Count Monitoring

Figure 6 shows the particle count trend for the treated water over one month at Springhurst. Several spikes can be seen where particle count increased significantly especially over the first week or two. These spikes were observed when a part of the system failed. When either the chlorine or the PAC pumping system failed Mn breakthrough was observed, and the breakthrough was monitored via the particle counter. When Mn concentrations were below 0.02mg/L particle count averaged around 400-800 particles/100ml and an increase from 0.02to 0.1mg/L resulted in particle counts up to 90,000 particles/100ml. Turbidity tracking was found to be less sensitive with Mn breakthrough tracking where increases in the range from 0.3ntu to 4ntu were seen at a maximum (Figure 7).

__Figure 6:__ ***Treated water particle count over time at Springhurst WTP***

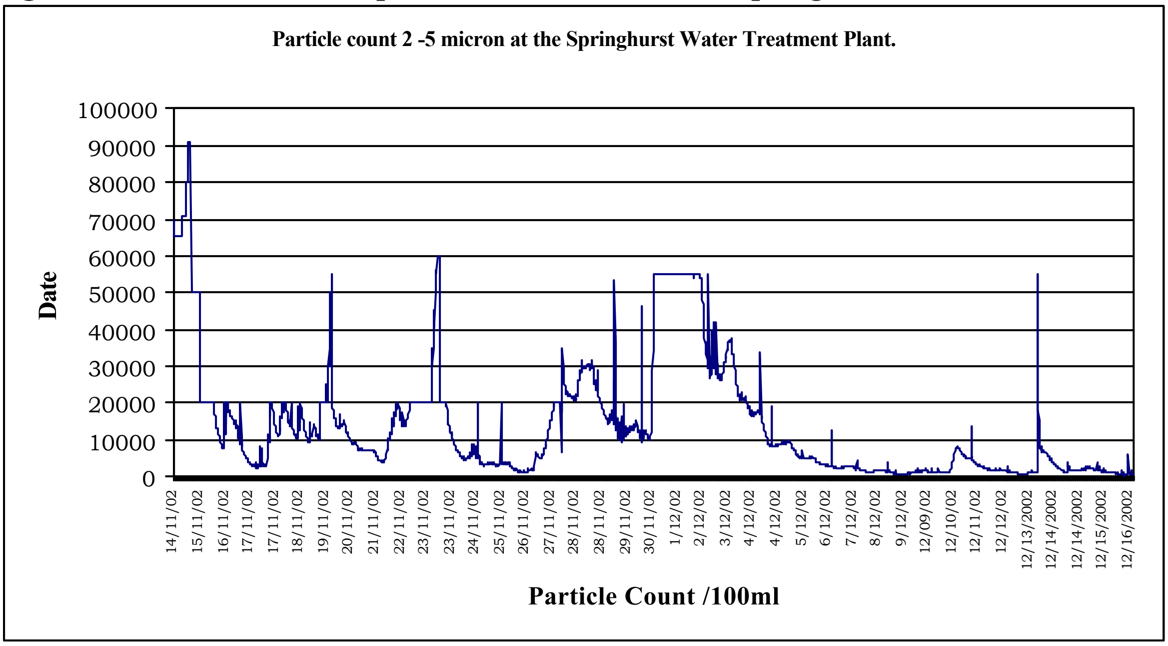
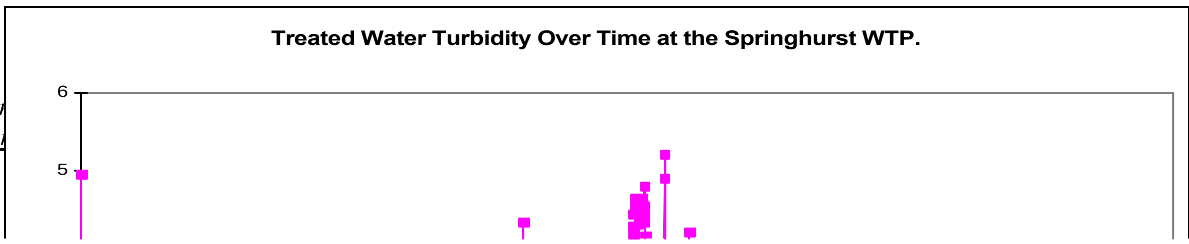



__Figure 7:__ ***Treated Water Turbidity over time at the Springhurst WTP***



## 4.0 COST OF TREATMENT

Throughout the duration of the exercise the extra cost of treatment has been as summarised in table 3 below. It can be seen that both increased costs via using chemicals not usually applied at the site and savings have occurred via reduced consumption of chemicals usually used.

**Table 3:** ***Additional cost of production ($/KL) for the manganese removal system compared to usual cost of Production. (un-shaded cells are based on normal operating parameters, shaded cells represent current dosing costs).***

| | Cl Post Dose (Kg) | Cl Pre dose (L) | Alum Dose (L) | Soda Ash Dose (Kg) | PACl Dose (L) | PAC Dose (Kg) |
|---|---|---|---|---|---|---|
| Volume Used | 40 | 1705 | 1580.049 | 350 | 210 | 80 |
| Cost/unit ($) | $1.826 | $0.35 | $0.222 | $0.39 | $2.29 | $1.00 |
| Total Cost | $73.04 | $596.75 | $350.77 | $136.50 | $480.90 | $80.00 |
| | | | | Total cost (1st 2 weeks of trial) | | $1,157.65 |

| | |
|---|---|
| Total cost (1st 2 weeks of trial) | $560.31 |
| Volume treated | 32391 |
| Normal Cost /kL | $0.0173 |

| | |
|---|---|
| Volume treated | 32391 |
| Total Cost /kL | $0.0357 |
| Additional cost/kL | $0.0184 |

It can be seen in table 3 that the additional expense of the manganese removal exercise was 1.84 cents per kL (total cost 3.5 cents/kL), which doesn't seem significant until compared to the original cost of treatment which was 1.73 cents/kL, this represents a doubling in the chemical cost involved in treatment.

The main contributing factor to this increase was the large quantities of Sodium Hypochlorite required to achieve adequate Mn removal, although the process that has been developed can be optimised somewhat to reduce this expense, as the time available for development and commissioning of the method was limited. It can also be noted that the additional cost of treatment derived from the PACl dosing is almost equally offset by the reduced need for pH correction that this flocculant allows where the cost of PACl was $180.13 more than the regular expense of Alum, however with no requirement for Soda Ash once river flows increased and raw water pH followed, only an additional $43.53 was required.

## 5.0 CONCLUSIONS

In conclusion the test work performed lead to NEW achieving high removal rates of Manganese via the addition of Chlorine and Powdered Activated Carbon. The cost of the new treatment method was found to be greater than regular modes of treatment however several benefits to the authority have been found throughout the investigation. These include what is so far an un-reported method of Mn removal which utilises PAC, the elimination of customer complaints regarding dirty water or staining of washing in Yarrawonga and the installation of the PAC dosing facility which can be utilised during summer months when taste and odour issues are often a cause for concern due to algae blooms.

At Springhurst the system developed at Yarrawonga once again proved efficient with removing high levels of manganese and particle counting is also seen as a monitoring tool with plenty of potential in manganese affected water supplies. It is recommended from the findings of this report that more work be done to properly refine (or 'optimise') the process which could deliver a more efficient chemical dosing regime as methods utilised throughout this event focused on those which could be very quickly and easily incorporated into the treatment process as it stood and was limited by several factors. The system was installed as a 'temporary' item.