Technical Memorandum 10

Oxidation of Manganese (II) in Island Billabong Water

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the Alligator Rivers Region

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Hart, B.T., and Jones, M.J. (1984). Oxidation of manganese (II) in Island Billabong water. Supervising Scientist for the Alligator Rivers Region, Technical Memorandum 10.

Manganese (II) added to unfiltered Island Billabong water at pH 7 is significantly reduced in concentration, presumably by oxidation to MnO_x, in a few days. Experimental difficulties precluded a definitive conclusion that bacteria catalyse this oxidation process. However, there is strong circumstantial evidence that this is so. There was evidence of a time lag before oxidation commenced in the unfiltered solutions and this suggests that the bacterial population may require an activation period.

Oxidation of manganese (II) occurred in both filtered and unfiltered Island Billabong water at pH 9. The rate was considerably faster in the unfiltered water. In the filtered water the oxidation appeared to be autocatalytic. The oxidation mechanism in the unfiltered billabong water was not elucidated.

1 INTRODUCTION

Manganese is one of the metals predicted to increase substantially in the Magela Creek system as a result of the Ranger uranium mining operations at Jabiru. Pyrolusite (MnO_2) is used as an oxidant in the production of uranium oxide. Most of the manganese ends up in the Tailings Dam (concentrations approximately 50-100 mg/L) from where a small, but significant, amount may eventually enter the Magela Creek system. The main interest in this metal, apart from its toxicity at high concentration, is its ability to form a number of solid oxide forms (MnO_x). These are effective scavengers of other metals and may accumulate and transport them to sensitive locations where they may be released back to the water column.

There have been a number of studies on the oxidation of manganese (II) in natural waters (Morgan 1964, 1967; Nealson and Ford 1980; Wilson 1980; Hem 1981; Stumm and Morgan 1981; Sung and Morgan 1981; Chapnik et al. 1982; Emerson et al. 1982; Grill 1982; Burdige and Kepkay 1983; Diem 1983). Morgan (1964, 1967) has shown that, in sterile conditions, the rate is dependent on pH and that the reaction is autocatalylic. The rate expression, at 25°C, is:

$$-\frac{d[Mn(II)]_t}{dt} = k_1\,[Mn(II)]_t + k_2\,[Mn(II)]_t\,[MnO_x]_t \qquad (1)$$

where $k_1 = k'_1\,[O_2(aq)]\,[OH^-]^2$ with $k'_1 = 4 \times 10^{12}\ M^{-3}\ d^{-1}$

$k_2 = k'_2\,[O_2(aq)]\,[OH^-]^2$ with $k'_2 = 10^{18}\ M^{-4}\ d^{-1}$

Work by Diem and Stumm (1984) suggests that this rate law may be applicable only to solutions that are initially oversaturated with respect to $MnCO_3$ or $Mn(OH)_2$. They found that in homogeneous solution, not oversaturated with respect to $MnCO_3$ or $Mn(OH)_2$ and free from catalysts, Mn(II) remains unoxidised for periods of several years. This suggests that the first rate constant, k_1, in equation 1 may be significantly overestimated.

Recent studies on the oxidation of manganese in natural waters have shown oxidation rates orders of magnitude larger than in synthetic solutions (Chapnik et al. 1982; Emerson et al. 1982; Diem and Stumm 1984). The difference is generally ascribed to very efficient surface catalysis or bacterial mediation (Sung and Morgan 1981; Chapnik et al. 1982; Burdige and Kepkay 1983).

These studies are relevant to recent experiments which aimed to provide a better understanding of the behaviour of manganese added to Island Billabong waters (Hart et al. 1984). In these experiments the observed behaviour of manganese was consistent with very rapid oxidation (three days) of the added Mn(II), followed by sedimentation of MnO_x.

The experiments described in this present report were undertaken in an attempt to show (i) that rapid oxidation of Mn(II) could occur in Island Billabong waters where the pH was around 6 to 7, and (ii) that this oxidation was catalysed mainly by bacteria.

2 METHODS

Two sets of three experiments were undertaken, one set at pH 7 and the other at pH 9. Manganese (as $MnCl_2$) was added to three litres of Island Billabong water in a four litre acid-washed, plastic beaker. At each pH the billabong water was treated in three ways: (i) filtered through a 0.4 µm Nuclepore filter, (ii) not filtered, and (iii) not filtered, chloroform added. The billabong water was taken on 17 October 1983 and the experiments were started the next day. The solutions were stirred continuously with a teflon-coated magnetic stirrer bar. The pH of the solutions was measured using a Metrohm E604 pH meter, and adjustments were made when necessary by drop-wise addition of 2 M NaOH or 2 M HCl. The experiments were conducted in an air-conditioned room at 30°C.

Aliquots were taken (using an Antlia syringe-filtration apparatus) at regular intervals for the determination of total and filterable manganese concentrations. Samples for the determination of filterable manganese were filtered through acid-washed 0.4 µm Nuclepore filters. Aliquots were stored in 125 mL acid-washed plastic bottles and were acidified with 0.25 mL concentrated HNO_3 (Merck Suprapur). The initial concentration of manganese in the unfiltered billabong water was 26 µg/L and in filtered water it was 20 µg/L.

Manganese concentrations were determined using a Varian AA6 with background correction. Samples were quantified by comparison with a standard curve derived using a standard manganese solution (BDH) diluted with 0.5% HNO_3.

It was necessary to correct all samples for increases in concentration due to evaporation of the solution during the experiment. Measurements made over a one week period, on a stirred three-litre volume of water (Milli-Q), gave an evaporation rate of 270 mL/week. It was assumed that the evaporation rate was constant with time.

3 RESULTS AND DISCUSSION

The concentrations of filterable and total manganese, measured as a function of time, are given in Table 1. Figure 1 shows the variation in the concentration of filterable manganese with time for the three experiments conducted at pH 7, and Figure 2 the variation at pH 9. In the following discussion it is assumed that the filterable manganese is unoxidised manganese (II).

3.1 Experiments at pH 7

According to the autocatalytic rate law for the oxidation of manganese (II) the time needed for 50% oxidation, given an initial Mn concentration of 7×10^{-6} M (385 µg/L), would be around 2000 days. In the unfiltered Island Billabong water, the added manganese was oxidised at a much faster rate than this (Fig. 1). It took around nine days for the initial manganese concentration to be reduced by 50%. In this solution there was a time lag of two to four days during which the concentration of filterable manganese remained essentially constant. This time lag may represent the time required in this particular Island Billabong sample for the bacterial population to reach a sufficient level of activity.

There was no oxidation of the manganese (II) added to filtered Island Billabong water at pH 7 (Fig. 1). Over the 13 day experiment concentrations of both filterable and total manganese remained constant. Had oxidation occurred, the concentration of filterable manganese would have reduced with time. The concentration of filterable manganese was consistently about 6% less than the total manganese concentration, probably owing to very rapid uptake of some Mn^{2+} onto the walls of the plastic container. This small initial loss of manganese (II) was evident in all experiments (Table 1).

There was evidence of manganese (II) oxidation in the chloroform-treated, unfiltered billabong water (Fig. 1). The concentration of filterable manganese remained essentially unchanged for almost 8 days, but from that time until day 13, the concentration appeared to decrease dramatically.

TABLE 1 CONCENTRATIONS OF MANGANESE.

Treatment:	pH 7.0			pH 9.0		
	Time[a] (h)	[Mn] (µg/L) Total	[Mn] (µg/L) Filterable	Time[a] (h)	[Mn] (µg/L) Total	[Mn] (µg/L) Filterable
Filtered	0	400	370	0	350	340
	5.7	400	380	5.5	350	-
	11.8	400	380	11.7	350	330
	23.6	400	380	23.2	360	340
	47.6	410	390	47.5	350	330
	97.6	400	390	97.3	340	300
	169.9	400	370	169.7	300	300
	315.2	390	360	314.5	280	160
Unfiltered	0	390	350	0	400	340
	5.8	390	340	5.6	400	160
	11.9	380	350	11.7	420	200
	23.5	380	350	23.4	410	210
	47.5	390	350	47.5	370	240
	97.8	390	340	97.4	350	190
	169.9	330	250	169.9	360	110
	314.9	240	22	314.7	340	50
Unfiltered + chloroform	0	410	370	0	400	340
	5.8	410	380	5.6	410	330
	11.9	410	390	11.7	430	300
	23.6	420	370	23.3	400	240
	47.6	-	380	47.6	380	220
	97.7	420	380	97.4	340	190
	170.0	400	370	169.8	330	64
	314.9	250	40	314.5	400	33

[a] Sampling commenced between 0905 and 1030 h on 18 October 1983.
Time = 0 h sample was taken 10 min after the addition of the Mn solution.

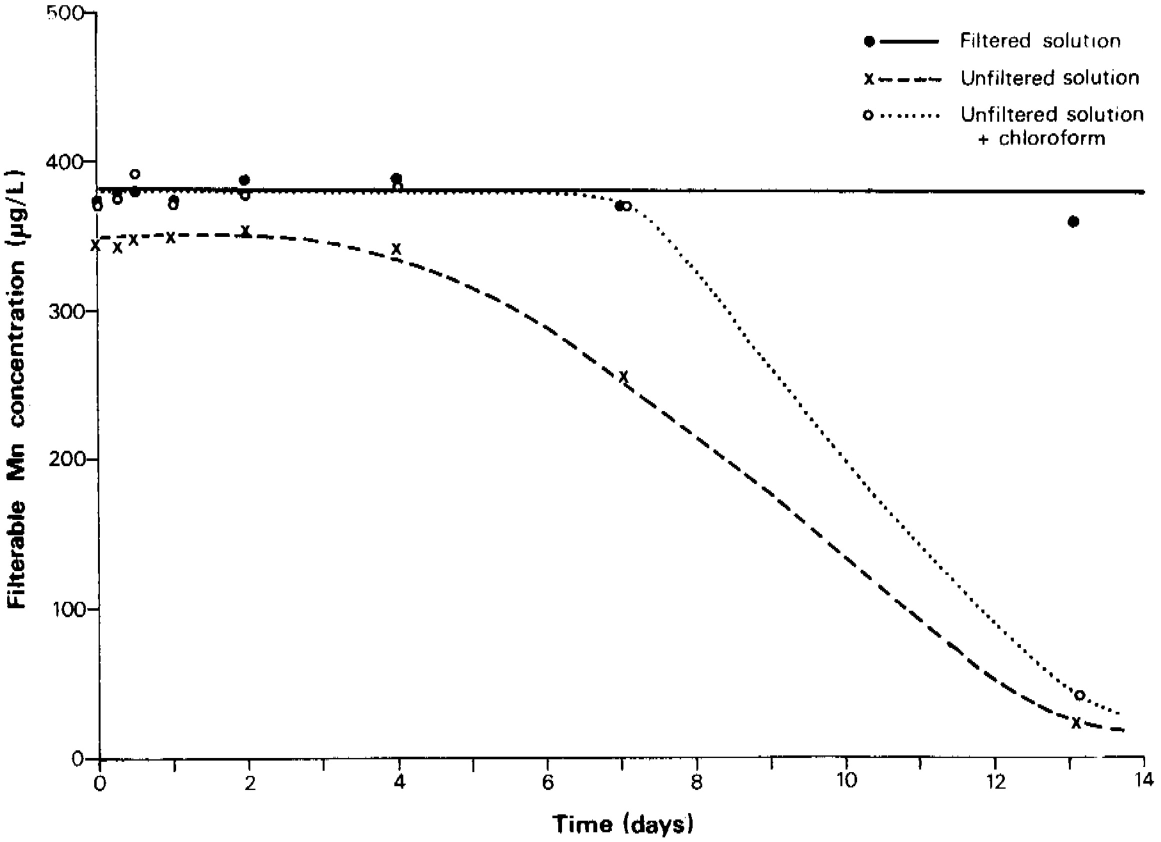

FIGURE 1 VARIATION IN THE CONCENTRATION OF FILTERABLE MANGANESE AT pH 7.

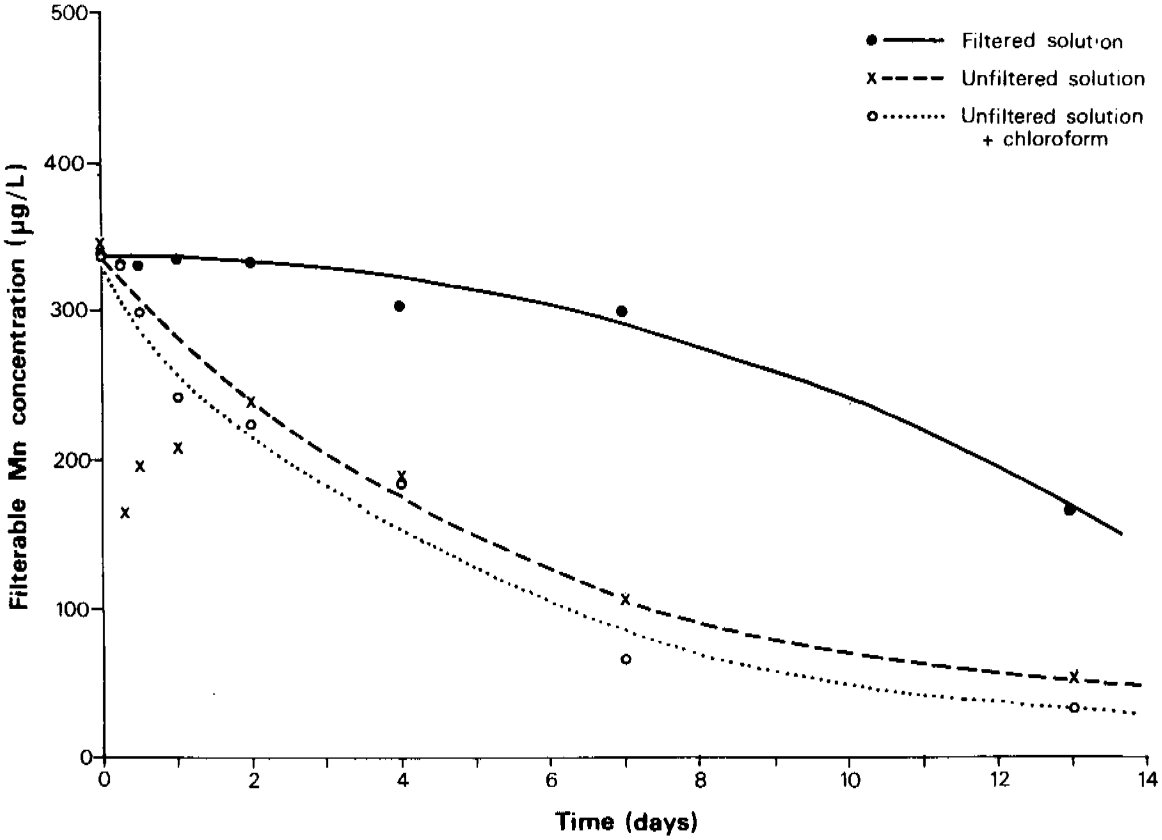

FIGURE 2 VARIATION IN THE CONCENTRATION OF FILTERABLE MANGANESE AT pH 9.

It should be noted that this observed decrease is based on only one experimental point. This apparent oxidation of manganese (II) is difficult to explain. If the chloroform had been effective in killing the bacteria, then oxidation due to this mechanism should not have occurred. It is possible that the chloroform was effective for a short period but then evaporated, owing to the high temperature of the experiment (30°C), allowing a bacterial population to establish and commence the oxidation.

The second possibility is that the surfaces of particulate matter could have catalysed the oxidation reaction. It is well known that certain solid surfaces can catalyse the oxidation of manganese (Couglin and Matsui 1976; Wilson 1980; Sung and Morgan 1981). However it is most unlikely that, at the very low concentrations of suspended solids in the Island Billabong water (approx. 1-2 mg/L), there would have been sufficient active surfaces to influence the rate significantly (Wilson 1980; Sung and Morgan 1981; Diem, pers. comm.).

In the two experiments where oxidation occurred (unfiltered, unfiltered + chloroform) the total concentrations of manganese were reduced with time. We believe this was due to the difficulty in sampling the solution after some brown MnO_x floc had formed. Just before each sampling the magnetic stirrer was turned to full speed in an attempt to make the solution as homogeneous as possible, but it seems that this was not totally successful. It is also possible that acidification of these samples, to a pH of around 1.5, is insufficient to dissolve the solid manganese oxide; a reducing agent may be required in addition to the acid.

3.2 Experiments at pH 9

Calculations using the autocatalysed rate equation (eqn 1) indicate that at this pH it should require two days for the initial manganese concentration to be reduced by 50%. The manganese (II) added to the filtered billabong water was oxidised over the experimental period, but at a slower rate than expected (it took around 12-13 days) (Fig. 2). This slower-than-expected rate is almost certainly due to the difficulties experienced with pH control in the solution. The pH was found to drift and had to be constantly readjusted. Over the period of the experiment the pH in this solution varied from 7.9 to 9.2 but was mostly in the range 8.5-9.0. The pH has a large influence on the rate of oxidation. Equation 1 predicts that at pH 8.5 the time for the initial manganese concentration to be reduced by 50% would be around 20 days compared with 2 days at pH 9.

The general trend in the reduction in the concentration of filterable manganese was similar in the unfiltered water and in the chloroform-treated water (Fig. 2). The rate of removal of filterable manganese was very much faster than in the filtered water. In the unfiltered water, the unexpected behaviour of the filterable manganese may have been associated with the difficulties in maintaining a constant pH (in the first four days the pH varied between 8.1 and 9.5) and with the fact that pH adjustment was by addition of 2 M NaOH or HCl. Diem and Stumm (1984) suggest that this method can lead, at least temporarily, to oversaturation in the solution in the region of the burette tip.

4 CONCLUSIONS

These experiments have shown that in unfiltered Island Billabong waters at pH 7 manganese (II) can be significantly reduced in concentration, presumably by oxidation to MnO_x, in a few days. Because of experimental difficulties, it is not possible to conclude definitely that bacteria catalyse this oxidation process. There is, however, strong circumstantial evidence that this is so. There was evidence of a time lag before oxidation commenced in the unfiltered solutions and this suggests that the bacterial population may require an activation period. If this is so, we expect that this time lag will vary throughout the year depending upon other processes occurring in the billabong at the time.

At pH 9, oxidation of manganese (II) in filtered billabong water appeared to be autocatalytic. However the rate of oxidation in the filtered water was considerably slower than in unfiltered water. Because of the very low concentration of particulate matter present in the unfiltered water it seems unlikely that surface catalysis could explain the difference. We are not able to comment upon whether or not bacteria are involved in the reaction at this higher pH.

A number of difficulties were experienced with these experiments. First, it was extremely difficult to maintain the pH constant at 9; this was less of a problem at pH 7. This pH variation, especially at the higher pH, would have had a considerable influence on the oxidation rate over the non-biologically catalysed pathway. In future we will investigate the use of a CO_2 buffered solution to maintain pH. Second, we are not happy with the use of chloroform as the bactericide, since at the temperature of the experiments it tended to evaporate. In future experiments sodium azide or some other chemical bactericide should be used.

The experience gained from these experiments will be used to design and conduct another series of experiments to more fully investigate the role of bacteria in catalysing the oxidation of manganese (II) in billabong waters.

5 ACKNOWLEDGMENTS

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