GLADSTONE NICKEL PROJECT ENVIRONMENTAL IMPACT STATEMENT SUPPLEMENT

Updated CSIRO Report

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Gladstone Pacific Nickel LTD

Manganese Oxidation in Port Curtis, Central Queensland

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Gladstone Pacific Nickel Limited

Commercial-in-confidence

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EXECUTIVE SUMMARY

Gladstone Pacific Nickel Limited (GPNL) is undertaking technical feasibility and environmental impact studies for the Gladstone Nickel Project (GNP). The GNP includes a nickel cobalt refinery that will treat high-grade nickel laterite ores imported from the South West Pacific, underpinned by beneficiated ores that will be piped in slurry form from GPNL's Marlborough deposits. The refinery is planned to be constructed and operated in two stages, with an ultimate capacity to produce some 8-10% of global nickel demand.

Recent predictions of plant operation indicate that the plant may discharge process waters into Port Curtis which could contain elevated concentrations of dissolved manganese. In order to understand the potential impacts of this development, it is necessary to assess the rate at which dissolved manganese will oxidise and thereby precipitate from solution. To address this question, a critical literature review was conducted (Apte 2006). The review indicated that there was little available data in the open scientific literature that could be used to accurately predict manganese oxidation rates in Port Curtis.

Initial field and laboratory studies conducted by CSIRO and Central Queensland University (Apte et al. 2007) indicated that the oxidation of dissolved manganese in the surface waters of Port Curtis may occur over timescales of weeks to months. It was noted that further work was required in order to accurately determine the rate of oxidation and also to understand the environmental factors affecting oxidation rates. This work also showed that oxidation rates at the sediment water interface were much faster. This was probably the result of bacterially-catalysed oxidation. It was recommended that further investigations be conducted in order to understand the rates of oxidation occurring at different benthic locations in Port Curtis and also understand the effects of manganese concentrations on oxidation rates.

In this current study, manganese oxidation rates were determined in the laboratory under controlled incubation conditions over a 6-week period. These experiments used waters from Port Curtis containing ambient suspended sediment concentrations supplemented with added inorganic manganese(II). The effect of suspended sediment concentration on oxidation rate was also investigated in a separate experiment. Benthic stirrer-reactors (Figure 1) were used to investigate the role of biological oxidation at the sediment-water interface at deep water and sub-tidal locations in Port Curtis representing different sediment types and deposition rates. Initially seven replicate cores (collected along with ca. 20 cm depth of overlying water) were taken at the front of mangrove stands in the mouth of the Calliope River. Additionally three replicate cores (collected along with ca. 20 cm depth of overlying water) were taken at a Middlebank, a deep harbour location (predominantly medium to coarse sand) and three cores on Wiggins Island seagrass meadows (mainly silt and clay with fine sand).

All studies were conducted jointly by the Centre for Environmental Contaminants Research, CSIRO Land and Water (CECR) and the Centre for Environmental Management (CEM) at Central Queensland University (CQU), Gladstone. Professor Barry Chiswell (NRCET) provided peer review and additional technical expertise. Laboratory and field incubation experiments were conducted in Gladstone and chemical analyses performed by CSIRO at their Lucas Heights laboratory, Sydney.

The findings of the study were as follows:

1. In laboratory incubations tests using manganese-spiked seawater conducted at a total suspended sediment concentration of 11 mg/L and water temperature of 26°C, the complete oxidation and precipitation of the added dissolved manganese (3000 µg/L) occurred within 21 days. The estimated half-life of dissolved manganese was between 10-11 days.

2. Incubation experiments conducted using seawater supplemented with additional sediment indicated that TSS concentration had little effect on the Mn oxidation rate over the range 11 to 67 mg/L of suspended solids.

3. Rapid oxidation of manganese(II) was observed in the benthic corer-reactor experiments using sediments collected from a mangrove-lined tidal mudflat region of Port Curtis and two other locations. Half lives of between 0.5 to 1.6 days were measured. These experiments further illustrate the important role of bacterial communities residing at the sediment-water interface in mediating the oxidation of manganese in estuarine systems.

4. The benthic corer-reactor experimental data was could be modelled by the heterogenous oxidation rate equation proposed by Morgan and co-workers. This provides a modelling approach for future studies.

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1 INTRODUCTION

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Recent predictions of plant operation indicate that the plant may discharge process waters into Port Curtis which could contain elevated concentrations of dissolved manganese. In order to understand the potential impacts of this development, it is necessary to assess the rate at which dissolved manganese will oxidise and thereby precipitate from solution. To address this question, a critical literature review was conducted (Apte 2006). The review indicated that there was little available data in the open scientific literature that could be used to accurately predict manganese oxidation rates in Port Curtis.

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In this current study, manganese oxidation rates were determined in the laboratory under controlled incubation conditions over a 6-week period. These experiments used waters from Port Curtis containing ambient suspended sediment concentrations supplemented with added inorganic manganese(II). The effect of suspended sediment concentration on oxidation rate was also investigated in a separate experiment. Benthic stirrer-reactors (Figure 1) were used to investigate the role of biological oxidation at the sediment-water interface at deep water and sub-tidal locations in Port Curtis representing different sediment types and deposition rates. Initially seven replicate cores (collected along with ca. 20 cm depth of overlying water) were taken at the front of mangrove stands in the mouth of the Calliope River. Additionally three replicate cores (collected along with ca. 20 cm depth of overlying water) were taken at a Middlebank, a deep harbour location (predominantly medium to coarse sand) and three cores on Wiggins Island seagrass meadows (mainly silt and clay with fine sand).

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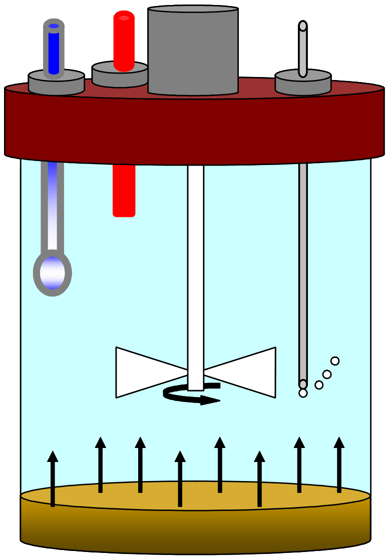

Figure 1. Schematic diagram of a benthic core stirrer-reactor.

2 EXPERIMENTAL

2.1 General Notes

All equipment required for the experiments was prepared at CSIRO Lucas Heights and transported to CQU Gladstone. Field work and execution of the experiments was conducted by a joint CSIRO/CEM team and commenced on 20 July 2007. The ambient seawater temperature during sample collection was 20ºC. The laboratory experiments were carried out 27ºC, the same incubation temperature used in the previous study in February, 2007 (Apte et al. 2007). Oxidation rates generally increase with increasing temperature, therefore, the higher temperature used in this study was adopted to represent a “worst case” scenario. All samples for chemical analysis were refrigerated and shipped to CSIRO for analysis.

2.1.1 Sample Collection

Seawater (7 x 20 L) for use in the long-term oxidation experiments and sediment cores from a mangrove area in the mouth of the Calliope River in Port Curtis were collected on 20 June, 2007. Additional sediment cores were collected one week later from Wiggins Island seagrass meadow and Middlebank (28 June, 2007).

2.1.2 Oxidation of Manganese in Seawater

Laboratory incubation experiments were conducted over a time scale of weeks in order to accurately determine the oxidation of manganese in the water column of Port Curtis.

A manganese(II) spiking solution (10,000 mg/L) was prepared by CSIRO prior to the commencement of the experiments. The manganese concentration of the spiking solution was checked by inductively coupled argon plasma emission spectrometry (ICP-AES) analysis prior to the start of the main experiments.

Seven bulk water samples (20 L) were collected in acid-washed carboys from a mid-channel location near Clinton Coal wharf and returned to the lab within 3 hours of collection. Water temperature was recorded at the time of sampling.

On return to the laboratory the carboys were shaken thoroughly (for at least 60 seconds) to ensure suspension of sediments. After shaking, Sub-samples (1 L) were then taken from each carboy for total suspended sediments (TSS) analysis.

A mud sample, collected at the mouth of the Calliope River in Port Curtis at low tide, was sieved through a coarse mesh (~ 1 mm diameter) to remove any large particles. A 50 g sub-sample of sieved sediment was weighed into a pre-weighed glass beaker and dried at 110 ^{o}C for 4 h, cooled and reweighed. The percent dry weight of the mud sample was used to calculate the mass of wet sediment to be added to 20 L seawater to increase the suspended sediment concentration by 100 mg/L (2 g dry sediment per 20 L). Wet sediment (3.4 g) was added to three 20 L carboys of seawater.

Three seawater-only carboys and the three carboys with added suspended solids were then spiked with the Mn(II) spiking solution. Six millilitres the Mn spiking solution (10,000 mg/L) was added to the six seawater solutions. The remaining carboy of seawater was left unspiked (blank treatment).

The samples were then incubated in the laboratory at the 27ºC, the ambient water column temperature recorded in the previous study in February, 2007. The carboys were gently shaken every 2-3 days to ensure saturation with dissolved oxygen (D.O). Each carboy was sampled weekly.

At each sampling event, each carboy was sampled for dissolved manganese, in duplicate, using a disposable plastic syringe and 0.45 µm pore size online filter. In order to pre-clean the filter, 20 mL of sample was filtered and discarded. The next 20 mL of filtrate was filtered directly into an acid-washed polycarbonate vial and retained for dissolved Mn analysis. Dissolved oxygen and pH were measured by carefully inserting the pre-washed probes into the surface waters of each carboy. Dissolved Mn samples were stored refrigerated prior to shipment to CSIRO for analysis.

2.1.3 Biological Oxidation of Manganese in Tidal Mangrove-lines Mudflats

Benthic core stirrer-reactors (Figure 1) were used to investigate the role of biological oxidation in an area of known fine sediment deposition. Further details of this experimental approach may be found in the publication by Jung et al. (2003).

Adsorption losses onto the surface of the stirrer-reactors may be problematic in these experiments, especially at low trace metal concentrations. Prior to the field work, an adsorption test was carried out at CSIRO. Triplicate reactors were filled with Mn-spiked seawater (10 µg/L and 100 µg/L) and losses of manganese from solution measured over 7 days. There was no statistically significant change in dissolved Mn concentrations was detected over the time course of the experiment indicating negligible adsorption losses. Full experimental results are given in Appendix 1.

Benthic core sampling locations are shown in Figure 2. Seven replicate cores (collected along with ca. 20 cm depth of overlying water) were taken at a mangrove location (77.2% <63 µm particle size), at the mouth of the Calliope River in Port Curtis at low tide on 20 July,

2007. This was the same site that cores were taken in the previous experiment (Apte et al. 2007). A 10 L surface water sample was also collected in an acid-washed carboy (for adjusting the water level in the corer reactors). The cores were transferred to the CEM laboratory in Gladstone as soon as possible and allowed to settle for several hours. The volume of the overlying water in each core was calculated and adjusted where necessary to 3.5 L. This was achieved by either removing water or topping up using the water collected from the sampling site.

A commercially available manganese(II) standard (1,000 ppm, Spectrosol) was used to spike the core reactors. Two of the cores were spiked with 30 µL of the Mn(II) standard to give final concentrations in the overlying water of ~10 µg/L. Two cores were spiked with 150 µL and another two cores spiked with 100 µL to give final concentrations of 50 and 100 µg Mn/L respectively. The remaining core was used as the experimental control (no Mn added).

The overlying water was gently stirred by a small motorised paddle in order to promote mixing of the water column. Oxygen was also bubbled in to the upper 2 cm surface water layer of each reactor using a plastic tube attached to an aquarium pump. The cores were incubated under controlled temperature conditions (27^{o}C). The sample treatments and sampling frequency was as follows:

Time	**Number of cores**			
	10 µg Mn/L	**50 µg Mn/L**	**100 µg Mn/L**	**Control[a]**
0	2	2	2	1
12 hour	2	2	2	1
1 day	2	2	2	1
3 day	2	2	2	1
5 day	2	2	2	1
7 day	2	2	2	1

[a] No added manganese

Small sub-samples (20 mL) were taken in duplicate at each sampling time. These sub-samples were immediately filtered using online syringe filters (0.45 µm) and retained for dissolved Mn analysis at CSIRO. TSS, pH and D.O. were also determined at the start and finish of the experiment.

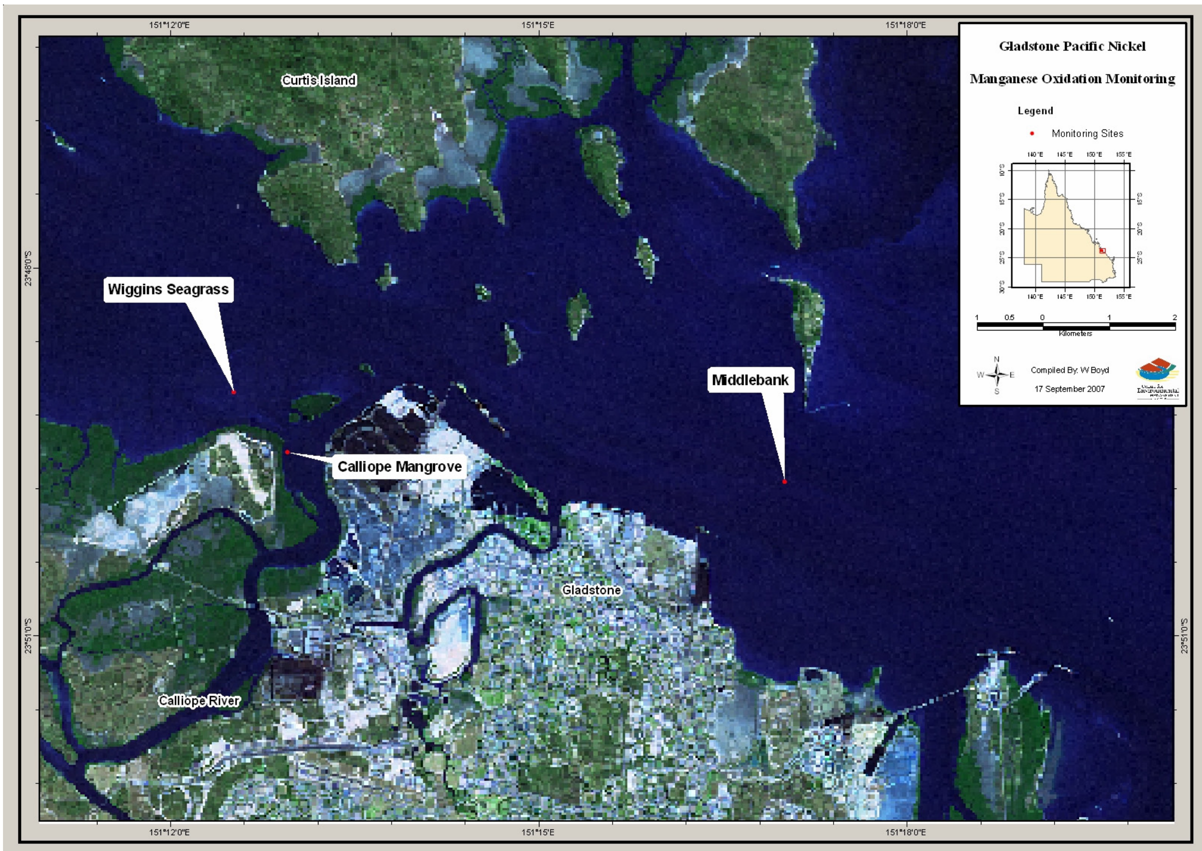

Figure 2. Locations of the benthic corer-reactor sampling sites.

2.1.4 Biological Oxidation of Manganese in Different Sediment Types

Benthic stirrer reactors were used to investigate the role of sediment type and manganese concentration on biological oxidation rate at the sediment-water interface. Three replicate cores were collected from Middlebank, predominantly coarse-sandy sediment (2.74% <63 µm particle size). Another three cores were collected from Wiggins Island seagrass meadow, predominantly silt and clay sediment with fine sand (68.6% <63 µm particle size). A 10 L surface water sample, from each site, was also collected in an acid-washed carboy (for adjusting the water level in the corer reactors). Upon return to the laboratory, two of the three cores from Middlebank were leaking. Leaks from one core stopped after sealing the base of the core with silicone sealant. The cores were allowed to settle over night before spiking with manganese.

The volume of the overlying water in each core was calculated and adjusted where necessary to 3.5 L. This was achieved by either removing water or topping up using the water collected from the sampling site. A 500 mL sub-sample was removed from each core reactors for analysis of TSS. Seawater from the collection site (500 mL) was added to each reactor to restore the water level to its original level.

Two of the cores from each site were spiked with 75 µL of the Mn stock solution (1,000 ppm) to give a final concentration of ~25 µg/L Mn(II). The remaining core from each site was used as the experimental control (no Mn added).

The cores were set up with individual stirrers, aerated and incubated (27ºC) as described above.

Time	Number of cores			
	Wiggins Island		Middlebank	
	25 µg/L	Control[a]	25 µg/L	Control[a]
0	2	1	2	1
12 hour	2	1	2	1
1 day	2	1	2	1
3 day	2	1	2	1
5 day	2	1	2	1
7 day	2	1	2	1

[a] No added manganese

Small sub-samples (20 mL) were taken in duplicate at each sampling time. These sub-samples were immediately filtered using online syringe filters (0.45 µm) and retained for dissolved Mn analysis at CSIRO. TSS, pH and D.O. were also determined at the start and finish of the experiment.

2.1.5 Analysis of Manganese and Total Suspended Solids

On receipt at CSIRO, the samples for Mn analysis were acidified by addition of ultrapure nitric acid (2 mL/L final concentration). Dissolved manganese concentrations were measured using inductively coupled plasma atomic emission spectroscopy (ICPAES) (Spectroflame EOP, SPECTRO Analytical Instruments, Kleve, Germany) calibrated with matrix-matched standards prepared from commercially-available standards (Plasma Chem, Farmingdale, NJ, USA). Laboratory blanks and analytical duplicates were included in each sample batch. Method detection limits (3 times the standard deviation of the blank measurements) and recoveries were calculated from this data. Total suspended solids were determined using a standard gravimetric procedure (APHA 1998).

3 RESULTS AND DISCUSSION

3.1 Oxidation of Manganese in Seawater

The experimental data for the laboratory incubation experiments are presented in Appendix 1 and the mean dissolved manganese concentrations summarised in Table 1 and Figure 3. The pH of the seawater in all treatments was 8.2. The suspended solids concentrations in the experiments are shown in Table 1. The full experimental data set is presented in Appendix 1 and mean concentrations in Table 2. As can be seen from the data, the agreement between the triplicate incubations was excellent. Manganese concentrations in the control treatment (no added Mn) were below the limit of detection (<2 µg/L) over the time course of the experiment.

Table 1. Suspended sediment concentrations of the incubation treatments

Sample	TSS (mg/L)
Control	3
Mn (II) spike – Replicate 1	12
Mn (II) spike – Replicate 2	11
Mn (II) spike – Replicate 3	10
Mean + Standard Deviation	11±1

Mn (II) spike + TSS – Replicate 1	64
Mn (II) spike + TSS – Replicate 2	66
Mn (II) spike + TSS – Replicate 3	70
Mean + Standard Deviation	67±3

The Mn spiked seawater experiments showed a slight loss of manganese in the first week of the experiment followed by rapid decline in dissolved Mn concentrations in the second week. After 1 week, a slight decrease in Mn concentration was observed with 94% of the initial Mn concentration detected. This was the same as the slight reduction in Mn concentration observed in the previous study where 6% reduction was measured (initial manganese concentration of 30 mg/L, ten times greater than this study) (Apte et al., 2007). There was then a rapid decline in dissolved Mn concentration in all replicate treatments and only 6% of the initial Mn added remained in solution after 2 weeks. The concentration of Mn in seawater with added suspended solids (67±3 mg/L) followed a similar trend with 83% and 6% of the initial Mn concentration measured after 1 and 2 weeks respectively. This indicated that suspended sediment concentration appeared to have little effect on manganese oxidation kinetics.

Black particulates were observed at week 2 in all of the Mn spiked carboys (with and without suspended solids). Sampling of all treatments continued until week 5 when it became obvious that dissolved manganese concentrations were below the analytical detection limit of 2 µg/L. The analytical data indicated that all added manganese had been oxidised and removed from solution by day 21 of the experiment.

Based on a simple graphical analysis of the experimental data, the half life of dissolved manganese was estimated at between 10 to 11 days. No further analysis of reaction kinetics was attempted owing to the lack of useable data (most data was below the detection limit).

Table 2. Mean Manganese(II) concentrations in the seawater oxidation experiment

Sample	Time (day)	Dissolved Mn (µg/L)	Standard Deviation
Blank	0	<2	–
	7	<2	–
	14	<2	–
	21	<2	–
	28	<2	–
	35	<2	–
Mn spike	0	2850	56
	7	2690	32
	14	156	255
	21	<2	–
	28	<2	–

	35	<2	–
Mn spike + suspended solids	0	2960	22
	7	2470	96
	14	167	631
	21	<2	–
	28	<2	–
	35	<2	–

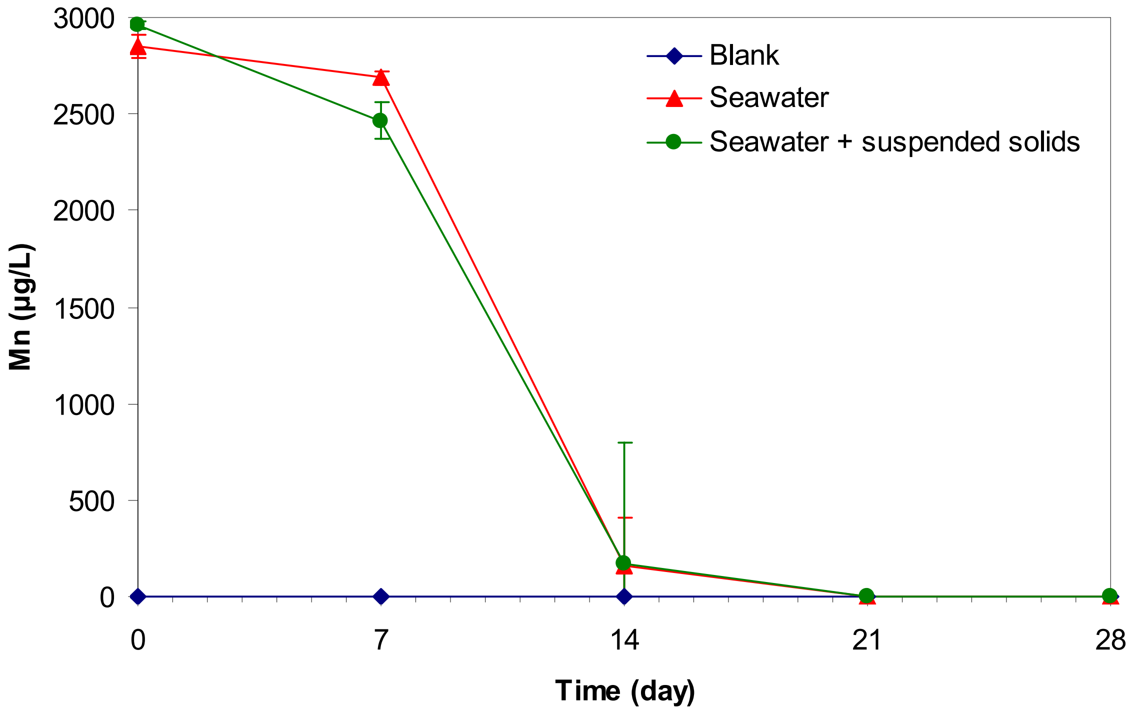

Figure 3. Variation of dissolved Mn concentrations with time during the long-term incubation experiments in seawater ± suspended solids (67±3 mg/L). Data points represent the mean of triplicate treatments. Data point for blank represents data from one replicate. Error bars show one standard deviation.

3.2 Benthic Sediment Studies

3.2.1 Tidal mangrove-lined mudflats

The first set of benthic core-reactor experiments were carried out with sediments collected from the same mangrove-lined mudflat location used in the previous study. Results for these experiments are summarised in Appendix 1 and graphically in Figure 4. The replicate cores of each added Mn treatments (10, 50 and 100 µg/L) were in good agreement and as a result, mean concentrations were used for graphing and calculation purposes. As can be seen from Figure 4 manganese concentrations declined rapidly in all experiments and were below background concentrations by day three. The half-life calculated for the 50 and 100 µg/L addition experiments was 1.6 days whereas the half life for the lowest Mn addition experiment (10 µg/L) was 0.6 days. These experiments confirm the results of the previous investigation using sediments from the same site (Apte et al. 2007). The results also compare favourably with the half lives of 19 and 32 hours measured in the previous experiment.

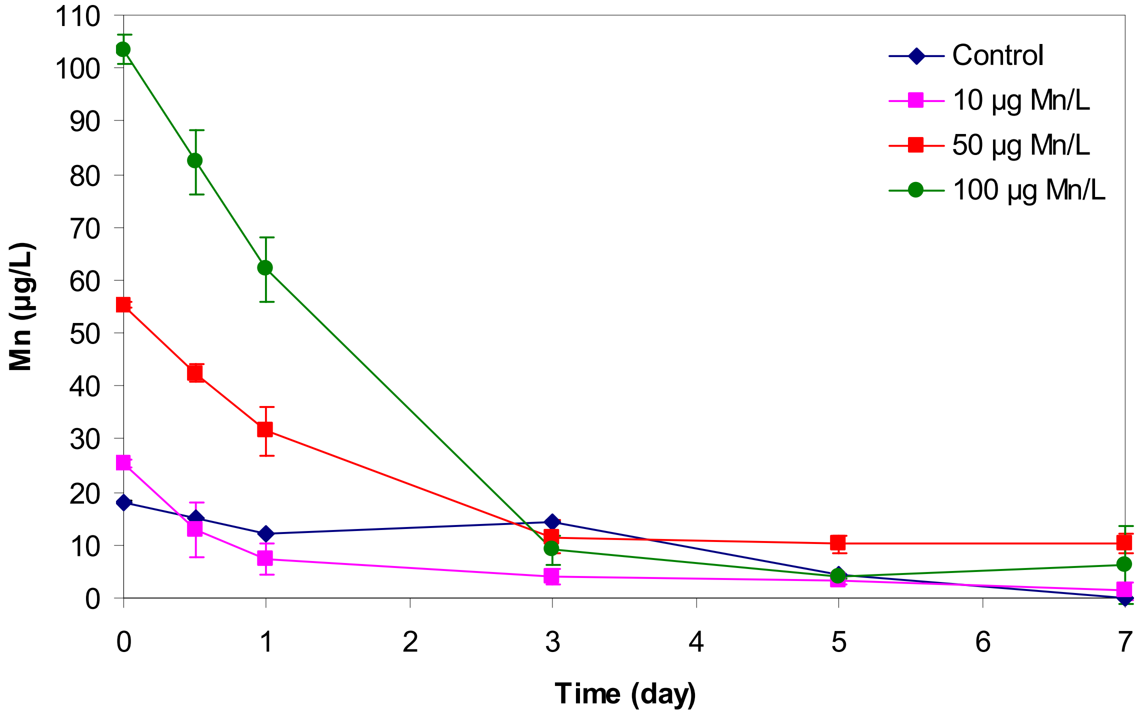

Figure 4. Change in dissolved Mn concentrations with time during the benthic corer-reactor experiments with sediments from tidal mudflats. Data points represent the mean of duplicate samples from two cores (n=4). Data point for Control represents the mean of duplicate samples from one core. Error bars show one standard deviation.

3.2.2 Middlebank and Wiggins Island sediment samples

The experimental data for the additional corer reactor experiments using sediments from the Wiggins Island seagrass beds and Middlebank sites are tabulated in Appendix 1 and shown graphically in Figure 5. Dissolved manganese concentrations in the controls, from both Wiggins Island and Middlebank, were below the limit of detection (<2 µg/L) over the 7-day incubation. Manganese concentrations in the replicate cores, for both sites, were variable and hence not combined for data analysis. There was a large reduction in Mn concentrations in Wiggins Island sediment after 12 h. Mn oxidation was more rapid in replicate 1 than replicate 2 after 24 h with no Mn measured in the replicate 1 core. The results for this core appear to be anomalous and are not discussed any further. For the Middlebank cores, the rate of decrease of dissolved manganese were similar over 7 days with approximately 50% decrease in Mn(II) after 1 day.

At both locations, manganese oxidation was rapid with dissolved manganese concentrations reducing to background concentrations within 5 days of incubation. These additional cores indicated that manganese oxidation at the sediment water interface is not just restricted to the mangrove lined areas of Port Curtis, but is significant at other benthic locations.

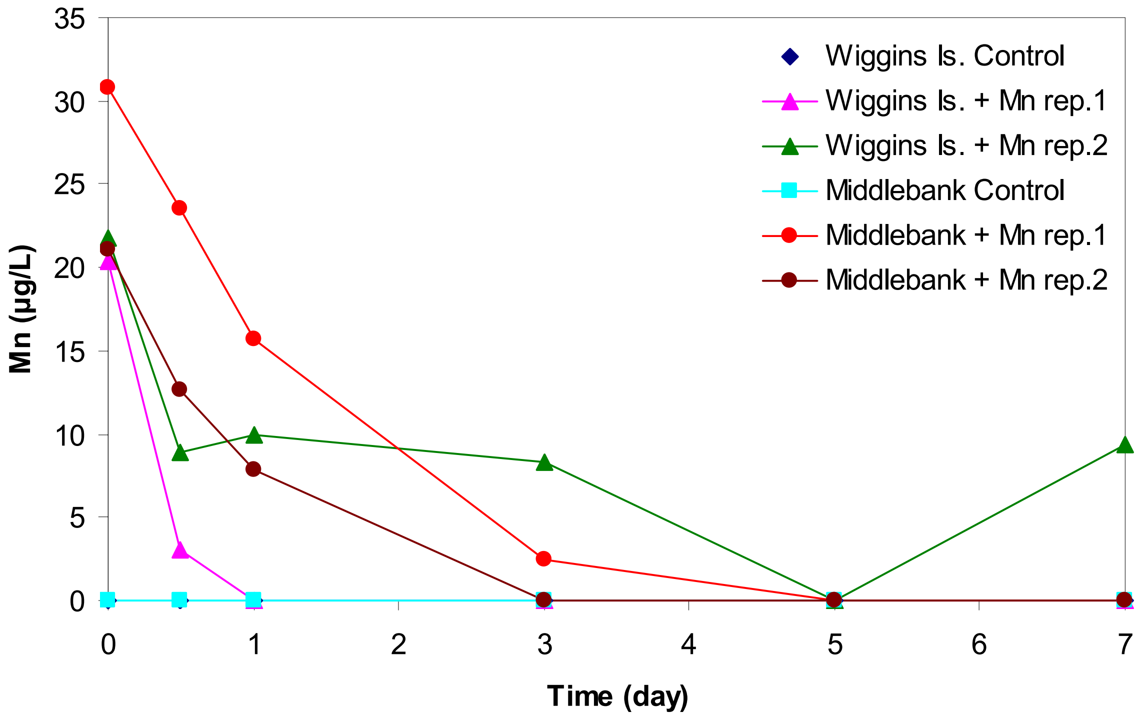

Figure 5. Variation of dissolved Mn concentration with time during the core-reactor experiments with sediment from Wiggins Island (seagrass bed, silt/clay sediment with fine sand) and Middlebank (coarse sand). Data from each individual core is shown. Each data point represents the mean of duplicate samples.

As indicated in our previous report (Apte et al. 2007), the heterogenous rate equation developed by Morgan and co-workers has utility as a tool for the prediction of dissolved manganese oxidation at the sediment-water interface. This is illustrated in Figure 6 which is a plot of all the stirrer-reactor data (but not including Wiggins Island replicate 2) against the concentrations predicted using the equation developed by Morgan. The constants k'1 and k'2 were adjusted by trial and error fitting. The final optimised values were k'1 = 0.03 (d^{-1}) and k'2 = 2.55 ($\mu m^{-1} d^{-1}$).This plot illustrates the utility of this kinetic equation in predicting Mn oxidation at the sediment water interface.

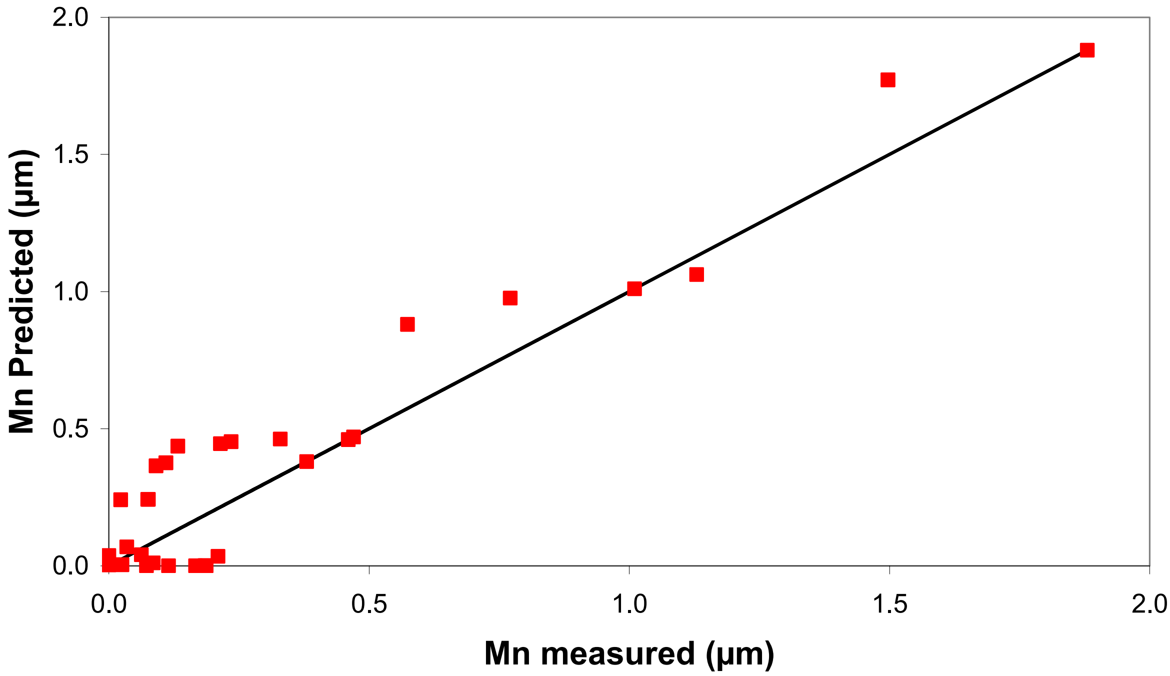

Figure 6. Benthic corer-reactor data plotted against dissolved manganese concentrations predicted using the Morgan heterogenous rate equation (y = 1.0254x + 0.0495, R2 = 0.9009). The solid line is the line of equivalence. If model predictions were perfect, all data would fit on this line.

4 CONCLUSIONS

1. In laboratory incubations tests using manganese-spiked seawater conducted at a total suspended sediment concentration of 11 mg/L and water temperature of 26°C, the complete oxidation and precipitation of the added dissolved manganese (3000 µg/L) occurred within 21 days. The estimated half-life of dissolved manganese was between 10-11 days.

2. Incubation experiments conducted using seawater supplemented with additional sediment indicated that TSS concentration had little effect on the Mn oxidation rate over the range 11 to 67 mg/L of suspended solids.

3. Rapid oxidation of manganese(II) was observed in the benthic corer-reactor experiments using sediments collected from a mangrove-lined tidal mudflat region of Port Curtis and two other locations. Half lives of between 0.5 to 1.6 days were measured. These experiments further illustrate the important role of bacterial communities residing at the sediment-water interface in mediating the oxidation of manganese in estuarine systems.

4. The benthic corer-reactor experimental data could be modelled by the heterogenous oxidation rate equation proposed by Morgan and co-workers. This provides a modelling approach for future studies.

5 ACKNOWLEDGEMENTS

The authors would like to thank Melissa Murphy and Rob Jung (CSIRO) for assistance with the preparation of the field equipment, James Charlesworth (CSIRO) for TSS measurements and Andrew Davis (CQU) for field work assistance. Professor Barry Chiswell, Queensland University, is thanked for his technical advice and peer review of this work.

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7 APPENDIX 1 - EXPERIMENTAL DATA

A. Adsorption study data

10 µg/L Mn Added

Replicate	Time (day)	Mn (µg/L)
A	0	10.4
B	0	10.4
C	0	10.6
Average		**10.4**
A	1	10.4
B	1	10.7
C	1	11.8
Average		**11.0**
A	7	9.5
B	7	9.8
C	7	12.4
Average		**10.6**

100 µg/L Mn Added

Replicate	Time (day)	Mn (µg/L)
A	0	100.7
B	0	102.9
C	0	103.4
Average		**102.3**
A	1	102.0
B	1	98.9
C	1	102.5
Average		**101.1**
A	7	102.0
B	7	102.2
C	7	103.6
Average		**102.6**

B. Long-term oxidation rate in seawater

(All Mn concentrations are in µg/L)

Sample	Day	Carboy 1		Carboy 2		Carboy 3		Mean	SD
		Rep. 1	Rep. 2	Rep. 1	Rep. 2	Rep. 1	Rep. 2		
Blank	0	<2	<2	-	-	-	-	<2	-
	7	<2	<2	-	-	-	-	<2	-
	14	<2	<2	-	-	-	-	<2	-
	21	<2	<2	-	-	-	-	<2	-
	28	<2	<2	-	-	-	-	<2	-
	35	<2	<2	-	-	-	-	<2	-
Mn (II) spike									
	0	2830	2870	2810	2970	2860	2860	2850	56
	7	2700	2670	2690	2620	2640	2700	2690	32
	14	<2	<2	14	13	461	449	156	255
	21	<2	<2	<2	<2	<2	<2	<2	-
	28	<2	<2	<2	<2	<2	<2	<2	-
	35	<2	<2	<2	<2	<2	<2	<2	-
Mn (II) spike + TSS									
	0	2960	2960	2980	2950	2960	3010	2960	22
	7	2470	2460	2620	2640	2430	2430	2470	96
	14	166	167	1390	1340	128	124	167	631
	21	<2	<2	<2	<2	<2	<2	<2	-
	28	<2	<2	<2	<2	<2	<2	<2	-
	35	<2	<2	<2	<2	<2	<2	<2	-

C. pH and Dissolved Oxygen Concentrations

Sample	Week	pH	D.O. (%)
Control	0	8.2	91
	1	8.2	71
	2	8.2	41
	3	8.2	78
	4	8.2	83
	5	8.1	75
Mn (II) spike – Replicate 1	0	8.2	84
	1	8.2	73
	2	8.0	32
	3	8.0	84
	4	8.0	86
	5	7.9	66
Mn (II) spike – Replicate 2	0	8.2	87
	1	8.2	78
	2	7.9	30
	3	7.9	85
	4	8.0	83
	5	7.8	69
Mn (II) spike – Replicate 3	0	8.2	77
	1	8.2	67
	2	8.0	30
	3	8.0	85
	4	8.0	81
	5	7.8	70
Mn (II) spike + TSS – Replicate 1	0	8.2	99
	1	8.2	57
	2	7.9	36
	3	7.9	88
	4	8.0	80
	5	7.8	69
Mn (II) spike + TSS – Replicate 2	0	8.2	99
	1	8.2	56
	2	8.0	32
	3	7.9	87
	4	7.9	76
	5	7.8	74
Mn (II) spike + TSS – Replicate 3	0	8.2	83
	1	8.2	59
	2	7.9	45
	3	7.9	88
	4	7.9	80
	5	7.8	69

D. Benthic Corer Reactor Experiments

(All Mn concentrations are in µg/L)

	Time (h)	Time (day)	Core A		Core B		Mean	SD
			Replicate 1	Replicate 2	Replicate 1	Replicate 2		
Control Core	0	0	18.3	18.1	–	–	18.2	0.14
	12	0.5	15.1	15.2	–	–	15.2	0.07
	24	1	–	12.2	–	–	12.2	–
	72	3	14.5	14.3	–	–	14.4	0.14
	120	5	4.2	4.3	–	–	4.3	0.07
	168	7	0	0	–	–	0.0	–
Low Mn	0	0	25.1	24.8	25.5	26.1	25.4	0.56
(~10 µg/L)	12	0.5	8.4	8.5	17.2	17.5	12.9	5.1
	24	1	4.8	4.7	9.7	9.9	7.3	2.9
	72	3	2.7	3.0	5.2	5.5	4.1	1.5
	120	5	2.5	2.8	4.2	4.2	3.4	0.90
	168	7	0	0	2.9	2.6	1.4	1.59
Medium Mn	0	0	55.9	54.5	55.4	55.4	55.3	0.58
(~50 µg/L)	12	0.5	41.3	40.7	44.4	43.1	42.4	1.7
	24	1	27.5	27.5	35.2	35.9	31.5	4.7
	72	3	9.1	8.4	13.8	14.8	11.5	3.2
	120	5	11.9	11	9.1	8.6	10.2	1.6
	168	7	12.4	11.4	8.3	9.0	10.3	1.9
High Mn	0	0	101	102	104	107	103.5	2.6
(~100 µg/L)	12	0.5	86.7	87.9	76.1	78.3	82.3	5.9
	24	1	67.4	67.4	56.3	57.1	62.1	6.2
	72	3	6.5	7.1	11	12	9.2	2.8
	120	5	3.7	4.0	4.3	3.9	4.0	0.25
	168	7	12.7	12.5	0	0	6.3	7.3

Where zero (0) is reported, the Mn concentration is below the limit of detection (<2 µg/L)

E. Wiggins Island Seagrass Beds and Middlebank Sites

Site	Time (h)	Time (day)	Core A		Core B		Mean	SD
			Replicate 1	Replicate 2	Replicate 1	Replicate 2		
Wiggins Island	0	0	21.4	19.3	20.3	23.2	21.1	1.7
	12	0.5	3.1	3.1	8.9	9.0	6.0	3.4
	24	1	0	0	10.1	9.8	5.0	5.7
	72	3	0	0	8.4	8.3	4.2	4.8
	120	5	0	0	5.7	<2	1.9	3.3
	168	7	0	0	9.5	9.2	4.7	5.4
Control Core	0	0	<2	<2			<2	0
	12	0.5	<2	<2			<2	0
	24	1	<2	<2			<2	0
	72	3	<2	<2			<2	0
	120	5	<2	<2			<2	0
	168	7	<2	<2			<2	0

Site	Time (h)	Time (day)	Core A		Core B		Mean	SD
			Replicate 1	Replicate 2	Replicate 1	Replicate 2		
Middlebank	0	0	29.9	31.6	22.5	19.7	25.9	5.7
	12	0.5	23.4	23.6	13	12.4	18.1	6.2
	24	1	16.2	15.2	8.0	7.7	11.8	4.6
	72	3	2.5	2.5	0	0	1.3	1.4
	120	5	0	0	0	0	0.0	0.0
	168	7	0	0	0	0	0.0	0.0
Control Core*	0	0	<2	<2			<2	0
	12	0.5	<2	<2			<2	0
	24	1	<2	<2			<2	0
	72	3	<2	<2			<2	0
	120	5	<2	<2			<2	0
	168	7	<2	<2			<2	0

Wiggins Island (seagrass bed)
Middlebank (coarse sand)
* Significant loss of water (leak) from core reactor during the experiment
Where zero (0) is reported, the Mn concentration is below the limit of detection (<2 μg/L)

Corer-reactor experiments: Oxygen, pH and TSS data

Sample	**Time**	**pH**	**D.O. (%)**	**TSS (mg/L)**
Control Core	0 h	8.2	83	14
	7 day	8.1	75	33
Low Mn (~10 µg/L) – Rep 1	0 h	8.2	86	10
	7 day	8.1	74	45
Low Mn (~10 µg/L) – Rep 2	0 h	8.2	89	
	7 day	8.0	64	2.4
Medium Mn (~50 µg/L) – Rep 1	0 h	8.2	88	
	7 day	8.9	58	36
Medium Mn (~50 µg/L) – Rep 2	0 h	8.2	79	6.9
	7 day	8.0	65	4.8
Medium Mn (~100 µg/L) – Rep 1	0 h	8.2	85	12
	7 day	7.9	63	50
Medium Mn (~100 µg/L) – Rep 2	0 h	8.2	91	9.5
	7 day	8.2	76	41

Sample	**Time**	**pH**	**D.O. (%)**	**TSS (mg/L)**
Wiggins Island – Control Core	0 h	8.2	69	94
	7 day	8.1	60	46
Wiggins Island (~25 µg Mn/L) – Rep 1	0 h	8.2	59	65
	7 day	8.0	51	7
Wiggins Island (~25 µg Mn/L) – Rep 2	0 h	8.2	49	44
	7 day	8.0	36	23
Middlebank – Control Core*	0 h	8.3	65	3.5
	7 day	8.4	54	2.5
Middlebank (~25 µg Mn/L) – Rep 1	0 h	8.3	70	3.3
	7 day	8.3	52	1.2
Middlebank (~25 µg Mn/L) – Rep 2	0 h	8.3	63	8.5
	7 day	8.3	62	4

* Significant loss of water (leak) from core reactor during the experiment

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