Manganese Oxidation Study

Simon C. Apte, Merrin S. Adams, Felicity Melville[1], Leonie Andersen[1] and Leigh T. Hales

Centre for Environmental Contaminants Research,

CSIRO Land and Water

[1]Centre for Environmental Management, Central Queensland University, Gladstone

Prepared for Gladstone Pacific Nickel Limited

CSIRO Land and Water Science Report 12/07

March 2007

Table of Contents

1. Background 5
2. Methodology 6
2.1. General Notes 6
2.2. Sample Collection 6
2.3. Laboratory Experiment 6
2.4. Field Incubation Tests 7
2.5. Biological Oxidation of Manganese in Tidal Mangrove-lined Mudflats 8
2.6. Laboratory Analysis 8
3. Results 9
3.1. Laboratory and Field Oxidation Experiments 9
3.2. Benthic Sediment studies 11
3.3. Oxidation Kinetics 12
4. Conclusions 15
5. Recommendations 16
6. Acknowledgements 16
7. References 16
Appendix 1 Preparation of the Synthetic Liquor 17
Appendix 2 Laboratory Data: Dissolved Mn Concentrations 18
Appendix 3 Suspended Solids, pH and Dissolved Oxygen Data. 19
Appendix 4 Benthic Core Reactor Data: Dissolved Mn Data 20

List of Figures

Figure 1. Schematic diagram of a benthic core stirrer-reactor. 6

Figure 2. Deployment of the spiked seawater samples for field incubation in Port Curtis. 9

Figure 3. Variation of dissolved Mn concentration with time during the incubation experiments. Each data point is the mean of triplicate treatments. Error bars are shown (often smaller than the actual data point). 11

Figure 4. Set-up of the benthic corer-reactor experiments in the CEM Laboratory, Gladstone. 12

Figure 5. Change in dissolved Mn concentration with time during the benthic corer-reactor experiments. 12

Figure 6. Benthic corer reactor data: first order oxidation kinetics plot (X = $[Mn_{initial}]/[Mn_t]$). 13

Figure 7. Heterogenous oxidation kinetics model. The solid lines are the fitted oxidation model data for the corer-reactor experimental data (Core A in blue and Core B in red). 15

List of Tables

Table 1. Laboratory incubation experiments: dissolved Mn concentrations 10

Table 2. Field incubation experiments: dissolved Mn concentrations 10

Table 3. Rate constants used in the heterogenous oxidation model 14

Executive Summary

Gladstone Pacific Nickel Limited (GPNL) are 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. Recent predictions of plant operation indicate that the plant may discharge process waters into Port Curtis which could contain ppm 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.

In order to accurately predict the fate of manganese in Port Curtis arising from the proposed GPN discharge, it was therefore necessary to experimentally determine the oxidation rate of Mn(II) in seawater. This report details experiments conducted to assess the oxidation rate over timescales of up to 7 days. 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, Lucas Heights, Sydney.

The study was designed to range-find the timescale of Mn(II) oxidation in the water column of Port Curtis (hours/days vs weeks/months). Oxidation rates were determined in the laboratory under controlled incubation conditions over a seven day period. In situ incubations at a moored site in Port Curtis were conducted as a confirmatory check on the laboratory experiment. In addition, laboratory incubation experiments were conducted with both inorganic Mn(II) and a manganese-containing synthetic liquor typical of the proposed discharge. This comparative experiment was included in order to check for enhanced oxidation in the presence of other chemical components of the proposed discharge. The experiments used waters from Port Curtis containing ambient suspended sediment concentrations. The potential scenario of enhanced biological oxidation at the sediment-water interface in mangrove-lined tidal mudflats was also examined by using benthic corer-reactors.

The findings of the study were as follows:

1. In both laboratory and field incubations tests conducted at a total suspended sediment concentration of 35 mg/L and water temperature of 26^{o}C, the oxidation of dissolved manganese was slow. Less than 6% of the added manganese was lost from solution over the 7-day time period of the experiments. This indicates that the half-life of dissolved manganese originating from the proposed discharge is likely to be of the order of weeks to months.

2. Over the 7-day timescale of the laboratory experiment, there was no observable difference between the oxidation behaviour of dissolved manganese added as part of a synthetic liquor or as an inorganic Mn solution.

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. Half lives of 19 and 32 hours were measured in the two reactors. These experiments illustrate the important role of bacterial communities residing at the sediment-water interface in acerbating the oxidation of manganese in estuarine systems.

4. The observed experimental data was best modelled by the heterogenous model of Mn oxidation proposed by Morgan and co-workers. This provides a modelling approach for future studies.

1. Background

Gladstone Pacific Nickel Limited (GPNL) are 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 ppm 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. 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.

In order to accurately predict the fate of manganese in Port Curtis arising from the proposed GPN discharge, it is therefore necessary to experimentally determine the oxidation rate of Mn(II) in seawater. This report details experiments conducted to assess the oxidation rate over timescales of up to 7 days. 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, Lucas Heights, Sydney.

The study was designed to range-find the timescale of Mn(II) oxidation in the water column of Port Curtis (hours/days vs weeks/months). Oxidation rates were determined in the laboratory under controlled incubation conditions over a 7-day period. In situ incubations at a moored site in Port Curtis were conducted as a confirmatory check on the laboratory experiment. In addition, laboratory incubation experiments were conducted with both inorganic Mn(II) and a manganese-containing synthetic liquor typical of the proposed discharge. This comparative experiment was included in order to check for enhanced oxidation in the presence of other chemical components of the proposed discharge. The experiments used waters from Port Curtis containing ambient suspended sediment concentrations. The potential scenario of enhanced biological oxidation at the sediment-water interface in mangrove-lined tidal mudflats was also examined by using benthic corer-reactors (Figure 1).

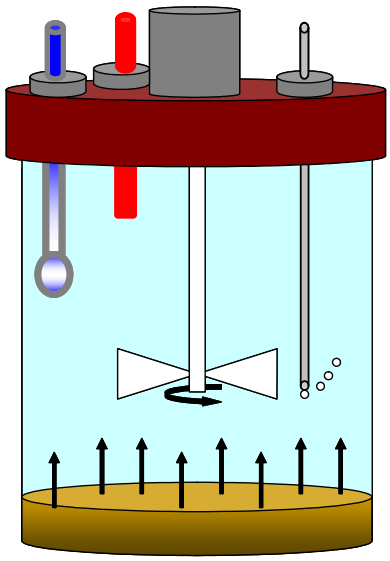


Figure 1. Schematic diagram of a benthic core stirrer-reactor.

2. Methodology

2.1. General Notes

All equipment required for the experiments was prepared at CSIRO Lucas Heights and transported to Gladstone. Field work and execution of the experiments was conducted by a joint CSIRO/CEM team between 5 and 12 February 2007. All samples for chemical analysis were refrigerated and shipped to CSIRO for analysis.

2.2. Sample Collection

A bulk water sample (60 L) was collected in acid-washed carboys from mid channel near Clinton Coal wharf and returned to the lab within 3 hours of collection. Water temperature was recorded at the time of sampling.

2.3. Laboratory Experiment

Manganese(II) spiking solution and synthetic liquor spiking solution were prepared by CSIRO prior to the commencement of the experiments. The synthetic liquor spiking solution was prepared according to predicted typical composition data supplied by GPNL (Appendix 1). The manganese concentration in this data is an order of magnitude higher than predicted typical discharge concentration. The manganese concentrations of the two spiking solutions were checked by inductively coupled argon plasma emission spectrometry (ICP-AES) analysis prior to the start of the main experiments. When spiked into seawater, the concentration of both solutions were sufficient to give Mn(II) concentrations realistic of the proposed discharge conditions (i.e. between 25-30 mg/L Mn).

On return to the laboratory the carboys were shaken thoroughly (at least 60 seconds) to ensure suspension of sediments. Three 1 L sub-samples were taken from the carboys for total suspended sediments (TSS) analysis.

Using a plastic measuring cylinder, 400 mL aliquots of the bulk sample were dispensed into 57 acid-washed 500 mL polyethylene bottles. During this operation, the bulk water sample was thoroughly shaken every 15 minutes in order to ensure suspension of sediments.
The solutions were then spiked with either inorganic manganese or the synthetic spiking solution. One millilitre of the inorganic Mn spiking solution (11,600 ppm) was added to 27 of the seawater solutions. The synthetic liquor spike solution was preheated to 50^{o}C (the predicted

discharge temperature) and 8.8 mL aliquots of the synthetic liquor spike solution were then added to 27 of the seawater solutions. The final solutions therefore contained 2.24% (v/v) of the synthetic liquor. The remaining 3 seawater solutions were left unspiked (blank treatments).

Following set up, the bottles were capped and gently shaken each day to ensure saturation with dissolved oxygen (D.O). The samples were then incubated at the ambient water column temperature (Ca. 27 ^{o}C) in the laboratory. The sampling frequency was as follows:

Time	Mn Spike (No. Samples)	Synthetic liquor spike (No samples)	Blank
0	3	3	-
1 hour	3	3	-
2 hour	3	3	-
4 hour	3	3	-
12 hour	3	3	-
1 day	3	3	-
3 day	3	3	-
5 day	3	3	-
7 day	3	3	3

At each sampling event, three bottles were sampled for dissolved manganese using a disposable plastic syringe and 0.45 µm pore size online filter. In order to preclean 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 on the remaining solutions. Dissolved Mn samples were stored refrigerated prior to shipment to CSIRO for analysis. The remaining contents of each bottle were then discarded.

2.4. Field Incubation Tests

This experiment followed a similar experimental set up as the laboratory experiment. In order to reduce the number of incubation bottles to be deployed in the field to a manageable number, the inorganic Mn(II) spike treatment only was used.

The solutions were prepared as described in section 2.3. The sample treatments and sampling frequency was as follows:

Time (Day)	Mn Spike (No. Samples)	Blank (No. samples)
0	3	-
1	3	-
2	3	-
3	3	-
4	3	-
5	3	-
6	3	3

The incubation bottles were set up in the laboratory and then returned to the field. The 24 bottles were moored in the mouth of the Calliope River adjacent to Wiggins Islands at a location in Port Curtis close to the proposed discharge point and three bottles were retrieved each day for 6 days. The samples were returned as quickly as possible to the laboratory (in a chilled esky) and sampled for dissolved Mn using the protocol described in section 2.3. The blank samples were sampled on the final day. TSS, D.O and pH were measured at the start and finish of the experiment.

2.5. Biological Oxidation of Manganese in Tidal Mangrove-lined 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). Three replicate cores (collected along with ca. 20 cm depth of overlying water) were taken at a mangrove location, at the mouth of the Calliope River in Port Curtis at low tide. 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 L. This was achieved by either removing water or topping up using the water collected from the sampling site.

Two of the cores (Core A and Core B) were spiked with 600 µL of a 1,000 ppm inorganic Mn(II) standard in order to increase Mn(II) concentrations to between 150-200 µg/L. This represents an upper limit dissolved manganese concentration for this region of Port Curtis (as predicted by recent hydrodynamic modelling based on the Appendix 1 discharge concentration, which is an order of magnitude higher than typical discharge concentration predicted by GPNL).

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	Core A	Core B	Control (no Mn added)
		(No. of samples)	
0	2	2	2
1 hour	2	2	2
2 hour	2	2	2
4 hour	2	2	2
12 hour	2	2	2
1 day	2	2	2
3 day	2	2	2
5 day	2	2	2
7 day	2	2	2

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 each experiment.

2.6. Laboratory Analysis

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, analytical duplicates and spiked samples 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

3.1. Laboratory and Field Oxidation Experiments

All field sampling including the collection of the benthic cores went as planned. The water temperature at the time of sampling was 26.8^{o}C. The total suspended solids concentration of the bulk water sample was 35±3 mg/L. Deployment of the field incubated solutions is shown in Figure 2.

Figure 2. Deployment of the spiked seawater samples for field incubation in Port Curtis.

Full experimental data for both the laboratory and field incubation experiments are presented in Appendices 2 and 3. The mean dissolved manganese concentrations are also summarised in Tables 1 and 2 and Figure 3. The experimental precision in these experiments was excellent with typically 3% relative standard deviation for the replicate treatments (n=3). Dissolved oxygen and pH were virtually constant throughout the course of the incubation experiments showing little evidence of systematic trends (Appendix 3).

As can be seen from Figure 3, dissolved Mn concentrations did not change appreciably over the duration of the experiments. In the inorganic Mn spike experiment, the mean concentration on day 7 was 94.1% of the day 1 concentration and in the synthetic liquor experiment the mean concentration on day 7 was 95.7% of the starting concentration. Overall, this indicated less than 6% oxidation of the added Mn over the time course of the experiment. The data was analysed statistically to see if these trends were actually significant. In order to improve statistical power, the initial concentration for each treatment was determined by pooling all measurements made during the first 12 h of the experiment. These were compared to the measurements made on the last day of the experiment. The final and initial dissolved Mn concentrations in both laboratory experiments were found to be significantly different (t test, $p<0.05$). It should be noted that most of the decline in concentration observed in the laboratory experiments occurred over the first 24 hours. In the field experiment (Table 2), there was no detectable oxidation of Mn(II) over the 6 day time course of the experiment.

Some caution should be added about the danger of over interpreting these results. Although there is evidence for some slight oxidation (ca. 5%) over the time scale of 7 days the data cannot be used to accurately determine oxidation rates. The experiments need to be conducted over much longer timescales ideally until greater than 50% of the dissolved Mn(II) is

oxidised. Nevertheless, it is reasonable to conclude that the half-life of Mn(II) in the waters of Port Curtis under the experimental conditions utilised, is of the order of weeks to months.

Table 1. Laboratory incubation experiments: dissolved Mn concentrations

Day	Hour	Mean	Standard deviation
Inorganic Mn Spike			
0	0	28.6	0.3
0.04	1	27.6	0.5
0.08	2	28.2	0.1
0.17	4	28.3	0.6
0.5	12	27.5	0.3
1	24	27.0	0.4
3	72	27.4	0.5
5	120	27.4	0.3
7	168	26.4	0.2
Synthetic liquor spike			
0	0	29.0	0.4
0.04	1	28.5	0.6
0.08	2	28.0	1.2
0.17	4	28.5	0.8
0.5	12	28.4	0.1
1	24	27.3	0.2
3	72	27.9	0.6
5	120	27.8	0.3
7	168	27.3	0.4

Table 2. Field incubation experiments: dissolved Mn concentrations

Day	Mean	Standard deviation
0	26.2	0.4
1	26.1	0.1
2	27.0	0.7
3	27.3	0.9
4	26.4	0.8
5	26.4	0.3
6	26.4	0.1

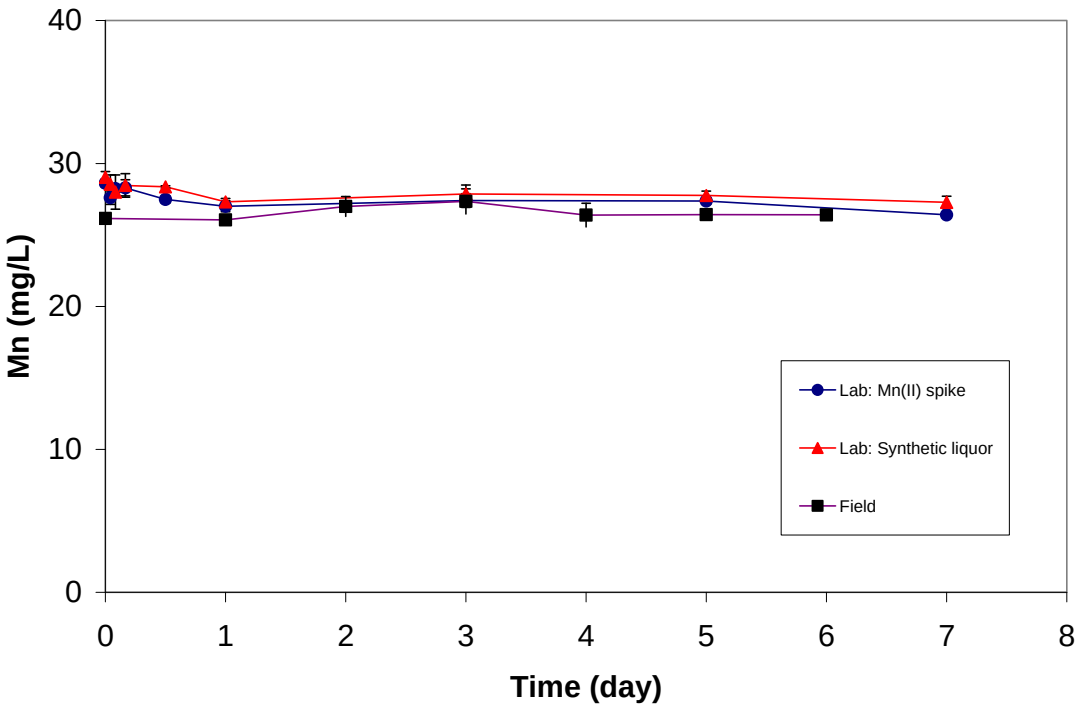


Figure 3. Variation of dissolved Mn concentration with time during the incubation experiments. Each data point is the mean of triplicate treatments. Error bars are shown (often smaller than the actual data point).

3.2. Benthic Sediment studies

The benthic reactor experiments are pictured in Figure 4. Full experimental data for these experiments are presented in Appendices 3 and 4. The duplicate samples taken for dissolved Mn analysis were in excellent agreement indicating good experimental precision. The mean dissolved Mn concentrations are summarised in Figure 5. Unlike the water column experiments, there was significant decrease in Mn concentration over the time course of the experiment. Indeed Mn was not detectable (<2 µg/L) after 7 days in both experimental treatments (Figure 5). Some differences between cores were observed. The half-lives of dissolved Mn in cores A and B were 32 and 19 hours respectively. Further experiments are required to understand the source of this variability. Interestingly, in the control treatment (no Mn added) the dissolved Mn concentration increased over the first day and was then relatively constant over the remainder of the experiment. The dissolved Mn concentrations in the spiked treatments actually dropped to concentrations lower than in the control. The trends in concentration were interpreted as evidence of the formation of insoluble oxidised Mn oxides in the experimental treatments which further catalyse the oxidation of dissolved Mn(II) (autocatalysis mechanism).

The results confirm the findings of the literature review (Apte 2006) that bacterial processes greatly enhance the oxidation kinetics of manganese(II). In estuarine systems, such processes are likely to be significant at the sediment-water interface.

Figure 4. Set-up of the benthic corer-reactor experiments in the CEM Laboratory, Gladstone.

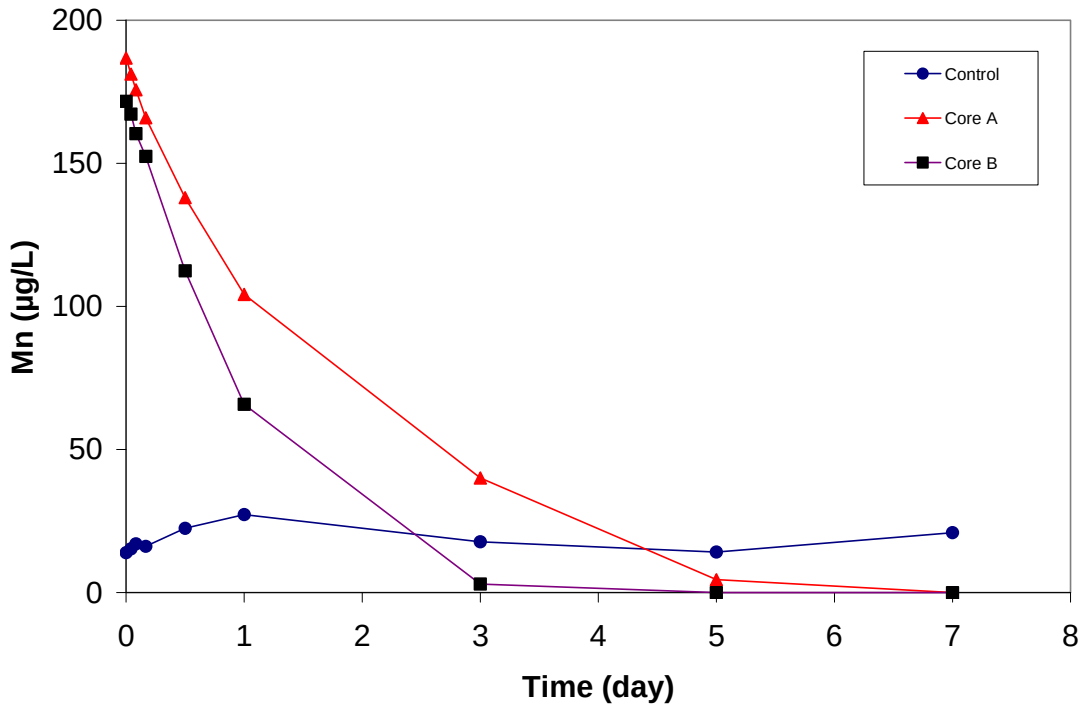


Figure 5. Change in dissolved Mn concentration with time during the benthic corer-reactor experiments.

3.3. Oxidation Kinetics

The experimental data obtained from the corer-reactor experiments were analysed in order to better understand the oxidation kinetics of manganese in these systems.

The homogenous oxidation of dilute Mn^{2+} in pure aqueous solution was shown by Morgan (2005 and references cited therein) to follow the rate equation:

$$-d[Mn^{2+}]/dt = k[Mn^{2+}][O_2]\,[OH^-]^2 \qquad (1)$$

In systems, where pH and dissolved oxygen concentrations can be considered constant, the concentration terms for these parameters can be incorporated into the rate constant k giving a much simpler pseudo first order expression:

$$-d[Mn^{2+}]/dt = k'[Mn^{2+}] \qquad (2)$$

The concentration of Mn^{2+} at time t may be calculated by integrating (2):

$$[Mn^{2+}]_t = [Mn^{2+}]_i\, e^{-kt} \qquad (3)$$

Therefore:

$$\mathrm{Ln}([Mn^{2+}]_t/[Mn^{2+}]_i) = kt \qquad (4)$$

Where:

k = conditional rate constant

$[Mn^{2+}]_i$ = initial concentration

$[Mn^{2+}]_t$ = concentration at time t

t = time

To test if the experimental data fitted this oxidation model, a plot of $\ln[Mn^{2+}]_i/([Mn^{2+}]_t$ vs time was constructed (Figure 6). If the reaction is first order, this plot should be a straight line. As seen, there is significant departure from linearity indicating that the observed experimental data cannot be adequately explained by this simple kinetic model.

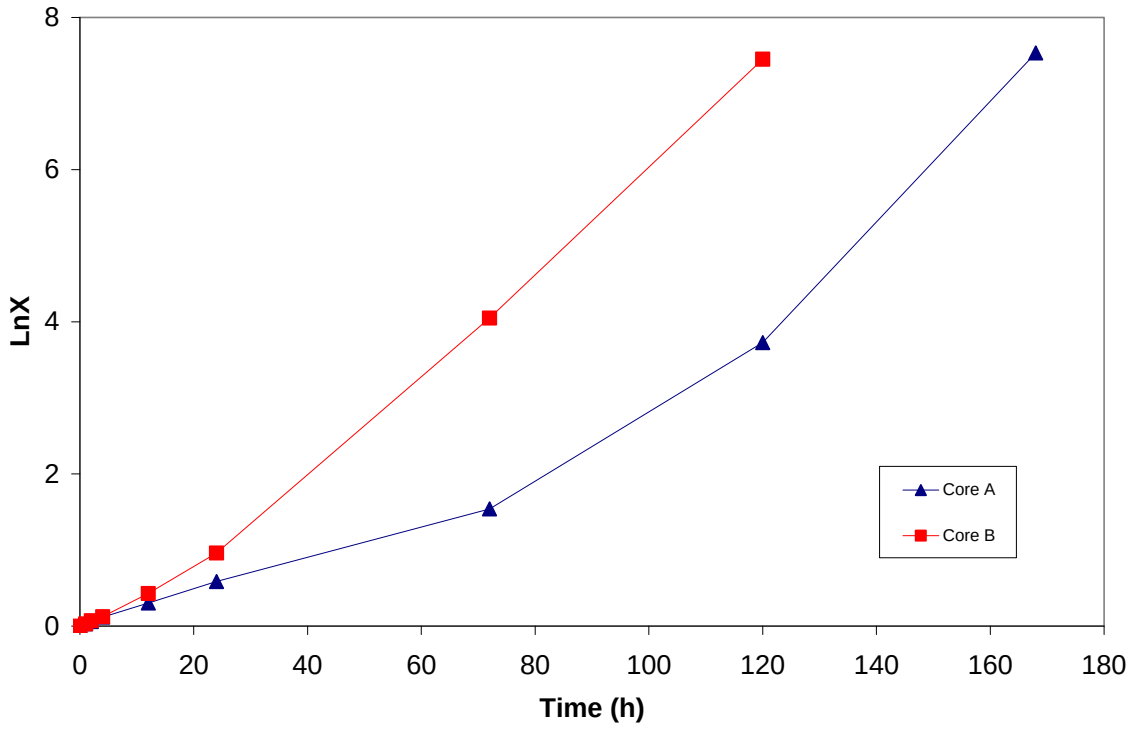


Figure 6. Benthic corer reactor data: first order oxidation kinetics plot ($X = [Mn_{initial}]/[Mn_t]$).

An alternative mechanism includes the autocatalysis of Mn(II) oxidation by particulate manganese (formed during the oxidation process) and other metal oxides (Morgan 2005):

$$-d[Mn^{2+}]/dt = k_1[Mn^{2+}][O_2] + k_2[Mn^{2+}][Mn_p][O_2] \qquad (5)$$

Where $[Mn^{2+}]$ is the molar concentration of dissolved manganese, $[Mn_p]$ is the molar concentration of particulate manganese and O_2 is the concentration of oxygen. The rate constants are both pH and temperature dependent and increase by a factor of 2 for every 11^{o}C increase in temperature (Yeats and Strain 1990). The above equation includes terms for both homogenous oxidation and heterogeneous autocatalysis. It should be noted that the concentration of particulate manganese is the 'autocatalytic' term. In natural waters however, this term is likely to also include bacterially mediated oxidation and oxidation involving other solids such as iron oxides.

In systems where dissolved oxygen is relatively constant, equation (5) simplifies to:

$$-d[Mn^{2+}]/dt = k'_1[Mn^{2+}] + k'_2[Mn^{2+}][Mn_p] \qquad (5)$$

Where k'_1 and k'_2 are conditional constants.

The integrated form of this equation is given in a paper by Sung and Morgan (1980):

$$[Mn^{2+}]_t = \frac{[Mn^{2+}]_0(k'_1 + k'_2[Mn^{2+}]_0)}{k'_2[Mn^{2+}]_0 + k'_1\exp[(k'_1 + k'_2[Mn^{2+}]_0)t]}$$

Their derivation is based on the assumption that $[Mn_p] = [Mn^{2+}]_0 - [Mn^{2+}]_t$. This equation can be used to predict the Mn(II) concentration at time t provided k'_1 and k'_2 are known. The equation was used to fit the benthic corer-reactor data presented in Figure 5. Initially, the k'_1 and k'_2 constants reported by Yeats and Strain (1990) were used and these were adjusted by trial and error to obtain the best fit of the experimental data. As can be seen from Figure 7, the actual fit of the heterogenous oxidation model against the experimental data is quite good. The fitted constants are presented in Table 3. The fitted constants for Core B are well within the range reported by other workers (Table 3). Overall, this demonstrates the utility of this kinetic expression in modelling the experimental data obtained from the benthic corer-reactor experiments.

Table 3. Rate constants used in the heterogenous oxidation model

Data Source	k'1 (d^{-1})	k'2 ($\mu m^{-1}d^{-1}$)
Yeats and Strain (1990)	0.04	1.28
Overnell et al. (2002)	0.03	1.05
This study: Core A	0.04	0.40
This study: Core B	0.04	1.00

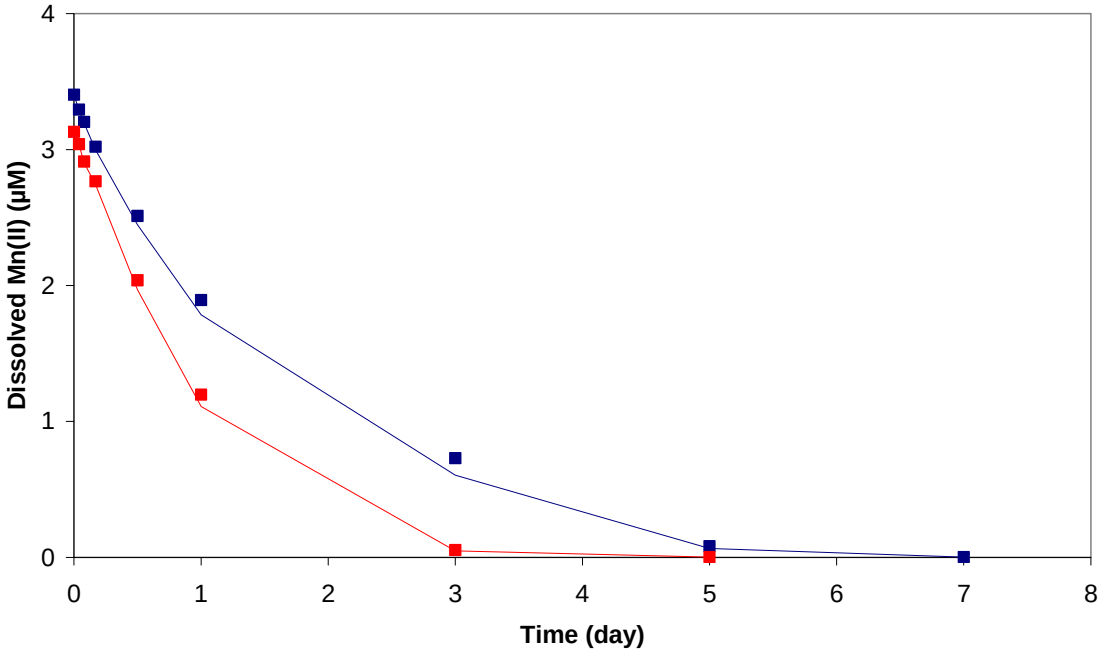


Figure 7. Heterogenous oxidation kinetics model. The solid lines are the fitted oxidation model data for the corer-reactor experimental data (core A in blue and Core B in red).

4. Conclusions

1. In both laboratory and field incubations tests conducted at a total suspended sediment concentration of 35 mg/L and water temperature of 26^{o}C, the oxidation of dissolved manganese was slow. Less than 6% of the added manganese was lost from solution over the 7-day time period of the experiments. This indicates that the half-life of dissolved manganese originating from the proposed discharge is likely to be of the order of weeks to months.

2. Over the 7-day timescale of the laboratory experiment, there was no observable difference between the oxidation behaviour of dissolved manganese added as part of a synthetic liquor or as an inorganic Mn solution.

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. Half lives of 19 and 32 hours were measured in the two reactors. These experiments illustrate the important role of bacterial communities residing at the sediment-water interface in accelerating the oxidation of manganese in estuarine systems.

4. The observed experimental data was best modelled by the heterogenous model of Mn oxidation proposed by Morgan and co-workers. This provides a modelling approach for future studies.

5. Recommendations

1. Long term incubation experiments should be conducted over a timescale of weeks in order to accurately determine the oxidation rate of manganese in the water column of Port Curtis.

2. Laboratory experiments should be conducted to examine the effects variables such as suspended sediment concentration and temperature on manganese oxidation rate.

3. The factors affecting the oxidation of manganese at the sediment-water interface should be investigated in more detail e.g. temperature and Mn concentration. The oxidation rate in deeper water benthic environments should also be determined.

6. Acknowledgements

The authors thank Rob Jung and Daniel Kilgore (CSIRO) for assistance with the laboratory studies, Andrew Davis (CQU) for field work assistance. Professor Barry Chiswell, Queensland University is thanked for his technical advice and peer review of this work.

7. References

APHA 1998. Standard Methods for the Examination of Water and Wastewater. 20th Edition. Washington, USA. American Public Health Association, Water Environment Federation, American Water Works Association.

Apte S.C. (2006). Manganese(II) Oxidation Rates in Seawater – A Review. Technical memorandum to URS. Prepared on behalf of Gladstone Pacific Nickel.

Jung, R.F., Jones, D.R. and Batley, G.E. (2003) Corer-reactors for contaminant flux measurements in sediments. J. Environmental Quality, 32, 1905-1910.

Morgan, J.J. (2005). Kinetics of reaction between O_2 and Mn(II) species in aqueous solutions Geochim Cosmochim Acta, 69, 2005, 35-48.

Overnell, J., Brand, W., Bourgeois, W. and Statham, P.J. (2002). Manganese dynamics in the water column of the upper basin of Loch Etive, a Scottish fjord. Estuarine Coastal and Shelf Science, 55, 481-492.

Sung, W. and Morgan, J.J. (1980). Kinetics and product of ferrous iron oxygenation in aqueous systems. Environmental Science and Technology, 14, 561-568.

Yeats, P.A. and Strain, P.M. (1990). The oxidation of manganese in seawater: rate constants based on field data. Estuarine Coastal and Shelf Science, 31, 11-24.

Appendix 1 Preparation of the Synthetic Liquor

Characteristics of Stage 1 Refinery Discharge (supplied by Gladstone Pacific Nickel Limited)

Parameter	Return Liquor	Cooling Water	Eductor Seawater	Discharge
Flow rate (m^3/h)	1,710	17,333	57,229	76,267
Density (kg/m^3)	1,079	1,021.1	1,024.5	1,025
Percent solids (%)	0.005%			0.00011%
Temperature (^oC)	50	38.5	23	27.1
pH	7	8.1	8.1	8.1
Ni (µg/L)	7,000			150
Co (µg/L)	1,000			20
Fe (II) (µg/L)	3,000	73	73	140
Mg (µg/L)	17,900,000	1,320,000	1,320,000	1,700,000
Al (µg/L)	2,000	69	69	110
Mn (µg/L)	1,300,000	8	8	29,000
Zn (µg/L)	40	1	1	1.9
Ca (µg/L)	670,000	411,000	411,000	420,000
Cl (µg/L)	12,080,000	19,400,000	19,400,000	19,300,000
SO_4 (µg/L)	66,400,000	2,688,000	2,688,000	4,100,000
H_2S (µg/L)	8,900			200

Synthetic liquor composition

One litre of synthetic liquor was prepared using the following recipe:

Major ions

Chemical added	Molecular mass	grams/L
$MgCl_2.6H_2O$	203.30	12.73
$MgSO_4.7H_2O$	246.37	166.1
$MnCl_2.4H_2O$	197.91	4.68
$CaSO_4.2H_2O$	172.17	2.88
NaCl	58.50	9.82

Minor constituents

Constituent	Liquor (mg/L)	Liquor (Molar)	mL of 1000 ppm std/L
Ni	7	0.000119	7.0
Co	1	0.000017	1.0
Fe(II)	3	0.000054	3.0
Al	2	0.000074	2.0
Zn	0.4	0.000006	0.4
H_2S	9	0.000261	9.0

Commercially-available 1000 ppm metal standards (Merck Spectrosol) were used. A 1000 ppm sodium sulfide solution was prepared from reagent grade sodium sulphide. The final pH of the synthetic liquor solution was adjusted to 7.0 by addition of sodium bicarbonate. The solution was heated to 50^oC prior to use in the experiments.

Appendix 2 Laboratory Data: Dissolved Mn Concentrations

All concentrations are in mg/L

Samples		**Replicate**				
	Day	**1**	**2**	**3**	**Mean**	**Std Dev.**
Field 0h	0	25.8	26.6	26.1	26.2	0.4
Field Expt Day 1	1	26.1	25.9	26.1	26.1	0.1
Field Expt Day 2	2	26.2	27.4	27.4	27.0	0.7
Field Expt Day 3	3	27.9	27.8	26.3	27.3	0.9
Field Expt Day 4	4	26.7	25.5	27.0	26.4	0.8
Field Expt Day 5	5	26.5	26.1	26.7	26.4	0.3
Field Exp Day 6	6	26.5	26.5	26.2	26.4	0.1
Field Blank Day 6	6	<2	<2	<2	<2	
Lab Spike 0h	0	28.4	29.0	28.5	28.6	0.3
Lab Spike 1h	0.04	27.9	27.9	27.1	27.6	0.5
Lab Spike 2h	0.08	28.2	28.2	28.3	28.2	0.1
Lab Spike 4h	0.17	28.9	27.8	28.2	28.3	0.6
Lab Spike 12 h	0.5	27.8	27.4	27.3	27.5	0.3
Lab Spike Day 1	1	27.2	26.6	27.3	27.0	0.4
Lab Spike Day 3	3	26.9	27.4	27.9	27.4	0.5
Lab Spike Day 5	5	27.4	27.1	27.6	27.4	0.3
Lab Spike Day 7	7	26.6	26.2	26.4	26.4	0.2
Lab Liquor 0h	0	29.1	29.4	28.6	29.0	0.4
Lab Liquor 1h	0.04	28.3	28.1	29.3	28.5	0.6
Lab Liquor 2h	0.08	28.5	26.6	28.9	28.0	1.2
Lab Liquor 4h	0.17	29.2	28.6	27.6	28.5	0.8
Lab Liquor 12 h	0.5	28.4	28.3	28.4	28.4	0.1
Lab Liquor Day 1	1	27.5	27.3	27.1	27.3	0.2
Lab Liquor Day 3	3	28.3	27.2	28.1	27.9	0.6
Lab Liquor Day 5	5	27.4	28.0	27.8	27.8	0.3
Lab Liquor Day 7	7	26.8	27.5	27.5	27.3	0.4
Lab Blank Day 7	7	<2	<2	<2	<2	

Appendix 3 Suspended Solids, pH and Dissolved Oxygen Data.

Field Experiment	**pH**	**D.O (mg/L)**	**TSS (mg/L)**
t=0	8.1	4.9	35±3
Day 1	8.2	5.3	-
Day 2	8.1	5.0	-
Day 3	8.2	5.1	-
Day 4	8.2	5.1	-
Day 5	8.2	5.1	-
Day 6	8.2	5.1	29.5
Field Blank, day 6	8.2	5.1	-

Lab Experiment			
	pH	**D.O (mg/L)**	**TSS (mg/L)**
Lab Liquor t=0	8.0	4.9	35±3
Lab Liquor t=1h	8.0	4.9	-
Lab Liquor t=2h	8.0	5.0	-
Lab Liquor t=4h	8.0	4.8	-
Lab Liquor t=12 h	8.0	4.9	-
Lab Liquor t=day 1	8.1	4.8	-
Lab Liquor t=day 3	8.1	4.8	-
Lab Liquor t=day 5	8.1	4.8	-
Lab Liquor t=day 7	8.1	4.8	-
Lab Spike t=0	8.1	4.8	35±3
Lab Spike t=1h	8.1	4.9	-
Lab Spike t=2h	8.1	5.1	-
Lab Spike t=4h	8.0	5.0	-
Lab Spike t=12 h	8.0	4.9	-
Lab Spike t=day 1	8.2	4.8	-
Lab Spike t=day 3	8.1	4.8	-
Lab Spike t=day 5	8.1	4.8	-
Lab Spike t=day 7	8.1	4.7	-
Lab Blank t=day 7	8.2	4.9	-

Corer-Reactor Experiment

Control (Core 3)	**pH**	**D.O (mg/L)**	**TSS (mg/L)**
Core 3 (Control) t=0	8.0	4.2	28
Core 3 (Control) t=day 7	8.0	4.2	7.8
Spiked Reactor 1 (Core A)	**pH**	**D.O (mg/L)**	**TSS (mg/L)**
Core 10 (Spike) t=0	8.1	4.3	17
Core 10 (Spike) t=day 7	8.0	4.9	9.6
Spiked Reactor 2 (Core B)	**pH**	**D.O (mg/L)**	**TSS (mg/L)**
Core 6 (Spike) t=0	8.1	4.3	36
Core 6 (Spike) t=day 7	8.1	4.6	5.6

Appendix 4 Benthic Core Reactor Data: Dissolved Mn Data

All concentrations are in µg/L

Control Core	**Time (h)**	**Time (day)**	**Mn Replicate 1**	**Mn Replicate 2**	**Mean**
0	0	0	14.0	13.9	13.9
1h	1	0.04	16.4	14.2	15.3
2h	2	0.08	16.1	18.0	17.1
4h	4	0.17	16.4	15.9	16.2
12h	12	0.5	22.6	22.3	22.5
day 1	24	1	27.3	27.3	27.3
day 3	72	3	18.0	17.5	17.8
day 5	120	5	14.0	14.3	14.2
day 7	168	7	20.9	21.0	21.0
Spiked Reactor 1 (Core A)			**Mn Replicate 1**	**Mn Replicate 2**	**Mean**
0	0	0	189	184	187
1h	1	0.04	182	180	181
2h	2	0.08	177	174	176
4h	4	0.17	166	166	166
12h	12	0.5	139	137	138
day 1	24	1	104	104	104
day 3	72	3	40.2	40.0	40.1
day 5	120	5	4.8	4.3	4.5
day 7	168	7	<2.0	<2.0	<2.0
Spiked Reactor 2 (Core B)			**Mn Replicate 1**	**Mn Replicate 2**	**Mean**
0	0	0	168	175	172
1h	1	0.04	168	167	167
2h	2	0.08	160	160	160
4h	4	0.17	153	152	152
12h	12	0.5	112	113	112
day 1	24	1	65.7	66.0	65.8
day 3	72	3	3.0	3.0	3.0
day 5	120	5	<2.0	<2.0	<2.0
day 7	168	7	<2.0	<2.0	<2.0

Marine Environment Reports

Appendix B5- Bioaccumulation of Manganese and Toxicity of Manganese Dioxide in Marine Waters

Bioaccumulation of Manganese and Toxicity of Manganese Dioxide in Marine Waters

J.L. Stauber and M.T. Binet

CSIRO Land and Water Science Report No 59/06

Prepared for URS Australia Pty Ltd

Commercial-in-confidence

December 2006

Enquiries should be addressed to:

Dr Jenny Stauber

61 2 9710 6808 or 852 23581399

Jenny.Stauber@csiro.au

Distribution list

Jenny Stauber	1
Monique Binet	1
Peter Collins	3 (1 e-copy, 1 hard)
Land and Water Library	1

Important Notice

Executive Summary

Gladstone Pacific Nickel Ltd (GPNL) is currently investigating the feasibility of developing a high pressure acid leach refinery to produce nickel and cobalt in the Yarwun Precinct of Gladstone, Queensland. The development will include a waste liquor-seawater discharge into Port Curtis. Preliminary test work and modelling has shown that the wastewater will contain manganese, and, due to poor tidal flushing in Port Curtis, concentrations of manganese may be above the current ANZECC/ARMCANZ (2000) guideline of 80 µg/L. A recent desk-top study by CSIRO critically summarised literature data on the toxicity of manganese(II) to marine biota and a revised water quality guideline of 140 µg/L was derived. However, additional information on the potential bioaccumulation and biomagnification of manganese, and on the toxicity of manganese oxides, was required to assess the overall risk of the proposed development.

The objective of this report was to summarise the available literature data on the toxicity of manganese dioxide (MnO_2) to marine biota and to determine the potential risk of bioaccumulation of all forms of manganese in marine biota.

Manganese bioaccumulation is common in most marine organisms, as manganese is an essential element. Manganese has been shown to bioaccumulate to higher levels in plants and invertebrates than in fish, with bioconcentration factors of up to 100,000, 55,000 and 100 respectively. Typical concentrations of manganese in algae, seagrasses, coral and invertebrates range from 5-50 µg/g, while tissues from marine fish contain 0.1-10 µg Mn/g. There is no evidence that manganese biomagnifies, i.e. increases in concentration at higher trophic levels.

Manganese is one of the least toxic metals to marine biota, with toxicity depending on its chemical speciation. In general, colloidal and particulate forms of manganese, such as MnO_2 have low bioavailability, whereas dissolved Mn(II) and Mn(VII), and organically bound manganese, are only toxic at mg/L concentrations.

Most studies on the mechanism of manganese toxicity have been carried out on freshwater species at concentrations well above that found in even the most polluted sites. In algae, manganese can affect chlorophyll synthesis, while in fish, manganese disrupts carbohydrate metabolism, haematological parameters and sodium and calcium metabolism, ultimately leading to oxygen deprivation. One marine study showed that manganese can cause suppression of the immune system in the Norway lobster (*Nephrops norvegicus*) exposed to 20 mg Mn/L for 10 days, potentially leading to an increase in the prevalence of infections in the lobster.

Very little additional information on the toxicity of manganese oxides was found. Only one report compared the toxicity of Mn(II) and Mn(IV) to the hatchability of brine shrimp. Although the authors concluded that Mn(IV) was more toxic than Mn(II), precipitation of manganese at all test concentrations (>10 mg Mn/L) confounded the results, and, in the absence of dissolved manganese measurements, it was not possible to attribute toxicity solely to MnO_2.

No published reports on the physical effects of manganese e.g. smothering or gill clogging could be found. However, under conditions of hypoxia, dissolved manganese is released from sediments and visibly precipitates on the gills and exoskeleton of the Norway lobster. The effect of the precipitated layer has not yet been investigated but the authors hypothesised that it may hamper normal function of the gills, leading to internal hypoxia. As in mammalian cells, dissolved manganese can accumulate in the brain, blocking nerve calcium channels of the nerve synapses, which may affect food search behaviour in lobsters.

Although manganese oxides appear to be of low toxicity to benthic biota, their low solubility, large surface area and favourable surface charge at the pH of seawater make them efficient scavengers of other trace metals. While this will potentially lower manganese availability to water column species, it may increase manganese availability to benthic biota that ingest

sediment particles. Manganese oxide coatings and attached metals may be dissolved in the guts of sediment-dwelling organisms (e.g tubificid worms), where pH and redox potential favour reducing conditions, rendering the metals available for uptake. Manganese oxides, and presumably metals adsorbed to them such as Pb, Co, Cu, Ni, Zn and Ag, appear to be more bioavailable than iron oxides.

Remobilisation of metals from manganese oxides in sediments back into the water column can also occur with changes in salinity, redox, lowered pH and increase in the concentrations of complexing agents. However, much of these released metals will be rapidly re-adsorbed to particulate material.

TABLE OF CONTENTS

Executive Summary **2**
Introduction **5**
Results and Discussion **5**
Manganese Speciation 5
Bioaccumulation of Manganese by Marine Biota 6
Mechanism of Manganese Toxicity 7
Toxicity of MnO_2 to Marine Biota 8
Effects of Manganese on Benthic Biota 9
Bioavailability of Metals Adsorbed to MnO_2 9
Remobilisation of Metals Adsorbed to MnO_2 9
Amelioration of Metal Toxicity by Manganese 10
Conclusions **10**
References **10**

Introduction

Gladstone Pacific Nickel Ltd (GPNL) is currently investigating the feasibility of developing a high-pressure acid-leach refinery to produce nickel and cobalt in the Yarwun Precinct of Gladstone, Queensland. A slurry pipeline will transport ore slurry from the nearby Marlborough mine to the Yarwun refinery. Neutralised residue from the Yarwun refinery will be stored in a residue storage facility in the Adolga area, close to Comalco's existing residue management area. After residue dewatering, the liquor will either be reused or surplus liquor combined with seawater cooling water and discharged via a diffuser to Port Curtis.

Preliminary test work and modelling has shown that the wastewater will contain manganese and, due to poor tidal flushing in Port Curtis, concentrations of manganese may be above the current ANZECC/ARMCANZ (2000) guideline of 80 µg/L. Habitats of concern in Port Curtis include mangroves and seagrasses (home of protected dugongs), principally along the southwestern shoreline, with corals more common on the eastern side of the Bay.

A recent desk-top study by CSIRO critically summarised literature data on the toxicity of manganese(II) to marine biota (Stauber, 2006). Using this data, a revised water quality guideline for manganese of 140 µg/L was derived to protect 95% of species with 50% confidence, according to the ANZECC/ARMCANZ (2000) approach (Stauber, 2006). However, additional information on the potential bioaccumulation and biomagnification of manganese is required to assess the overall risk of the proposed development.

Manganese(II) is slowly oxidised by bacteria in seawater to manganese dioxide (MnO_2). A recent desk-top study by Apte (2006) estimated that manganese oxidation rates in Port Curtis seawater should be slow, in the order of weeks to months. However, the potential toxicity (both chemical and physical) of MnO_2 is not known.

The objective of this report was to:

1. summarise the available literature data on the toxicity of MnO_2 to marine biota
2. determine the potential risk of bioaccumulation of all forms of manganese in marine biota.

Results and Discussion

Manganese Speciation

The toxicity of manganese is dependent on its chemical speciation, which in turn is dependent on water quality parameters. In reducing environments with a low pH, the thermodynamically favoured form of manganese is soluble manganese(II). In contrast, thermodynamic considerations suggest that manganese in aerated seawater should exist as insoluble MnO_2. However, filterable manganese (about 0.1 µg/L) usually exceeds particulate concentrations in open ocean seawater by an order of magnitude, suggesting that most is present as soluble manganese(II) (Huntsman and Sunda, 1980). This may be due to the extremely slow oxidation kinetics of manganese(II) in aerated waters as well as to the interaction of manganese(II) with dissolved organic matter, which hinders precipitate formation.

Oxidation of manganese is increased by increasing pH or by the presence of catalytic surfaces such as MnO_2. Bacteria also mediate manganese oxidation in natural waters to provide carbon from complex humic substances for growth. Manganese oxidation by bacteria also protects them from damage from other metals and UV light, and strengthens the bacterial capsule (Sunda and Kieber, 1994).

The other main mechanism affecting concentrations of manganese in the water column is adsorption/desorption reactions. Manganese is weakly adsorbed to crystalline iron oxides and other colloidal material (WSC/NSR, 1995).

As with most other metals, a range of inorganic ligands can also interact with manganese to form complexes such as $MnCO_3$, $MnSO_4$ and $MnOH^+$. Manganese only forms weak

complexes with organic ligands and organic complexation does not play a major role in controlling manganese speciation in natural waters.

Bioaccumulation of Manganese by Marine Biota

Although metals can affect organisms at the cell or gill surface, toxicity is usually manifested after the metal has been taken up into the organism. Bioconcentration is the accumulation of a metal in the tissue of an organism due to uptake of the metal from water, whereas bioaccumulation generally refers to metal uptake from food. Both can only take place when the rate of uptake exceeds the rate of elimination. Both processes depend on many factors including the concentration and speciation of the metal in the water and food, water quality characteristics, exposure time, tissue type and the age and physiological status of the organism.

Manganese is an essential element and is therefore actively taken up by both plants and animals. Bioconcentration factors (BCFs) range from 2000-100,000 for plants, 2500-6300 for phytoplankton, 300-5500 for marine macroalgae, 800-830 for mussels, and 35-930 for fish (WHO, 2004).

Plants

Manganese is readily concentrated in marine plants, with BCFs of up to 100,000 (WHO, 2004). Partial or complete regulation is achieved by most species within the range of manganese concentrations encountered in the natural environment (Stokes et al., 1988). Ichikawa (1961) recorded BCFs ranging from 300 for the seaweeds *Laminaria saccharina* to 7,500 for *Fucus serratus.* Goldberg et al. (1971) also reported BCFs for marine plants of about 3000.

Seven of twelve genera of seagrasses occupy tropical climates, including *Halodule*, *Cymodocea*, *Syringodium*, *Thallassodendrum*, *Enhalus*, *Thalassia* and *Halophila*. However, the majority of work on the bioconcentration of metals has been done on temperate species such as *Zostera* and *Posidonia*. Brinkhuis et al. (1980) found that eelgrass *Zostera marina* accumulates manganese in leaf tissues. The manganese was strongly retained in the cytoplasm of living cells. Seagrass leaves constitute a major transport pathway for the cycling of manganese between different media (Peters et al., 1997).

Manganese is likely to have limited impact on mangroves because mangroves are particularly good at sequestering metals and immobilising them in anoxic sediments. De Laune et al. (1981) found that metals, including manganese, are exported from mangroves via detritus. Nye (1990) estimated that 9130 kg of manganese was exported annually from mangrove forests in South Eastern Florida. Manganese concentrations in mangrove sediments ranged from 1-640 µg/g dry weight, with 0.4-500 µg/g in the red mangrove *Rhizophora* sp. and 5-31 µg/g in invertebrates.

Invertebrates

Manganese accumulation has been reported in a broad range of marine invertebrates, with a wide variation in bioaccumulation between species. Scallops appear to have the greatest ability to concentrate manganese, with BCFs up to 55,500 (Stokes et al., 1988).

Due to its chemical properties, manganese is found in highest concentrations in the calcified parts of crustaceans, namely in the exoskeleton, gills and the gastric mill of the stomach. Decapod lobsters such as *Nephrops norvegicus* contain more than 98% of the total manganese content in their exoskeletons and this manganese is believed to have little effect on the animals (Baden and Eriksson, 2006). Uptake of manganese from water via the gills is a more important route of exposure than sediment and food, as lobsters fed a diet high in manganese had similar tissue manganese concentrations as controls (Norstedt, 2004).

Ikuta and Nakahara (1986) measured manganese uptake in the perry whelk *Volutharpa ampullacea perryi*, a carrion feeder inhabiting shallow waters of the Pacific Ocean and Japan Sea. BCFs at steady state ranged from 800-1900, with a mean of 1330 ± 310 for females and 1450 ± 260 for males. Uptake of manganese was about 4-8 times higher than in black abalones.

Hansen and Bjerregaard (1995) found that dissolved ^{54}Mn was accumulated linearly with time in the sea star *Asterias rubens*, with a BCF of 19 after 23 days. Most manganese concentrated from water was found in external surfaces (tube feet, skin) whereas manganese accumulated from food was distributed in pyloric caeca. Assimilation efficiency from food was 69% and was higher than that from water.

One of the few reports of manganese accumulation in tropical invertebrates was by Khristoforova and Bogdanova (1981), who measured manganese concentrations in the tropical giant clam *Tridacna squamosa* collected from coral atolls in the South West Pacific. They found manganese concentrations were the same in clams from populated and unpopulated atolls. They found low concentrations of manganese in muscle (<0.05 µ/g), 3-4 µg/g in gills and 12-15 µg/g dry weight in liver.

Field transplant studies with oysters and barnacles illustrate how uptake, elimination and resulting tissue metal burdens in invertebrates may be dependent on age (size) and condition of the organism. For example, concentrations of manganese in oysters (*Crassostrea gigas*) attained steady state in 4 months after transplantation, while in larger individuals 5 months or more was required (Boyden and Phillips, 1981). Seasonal variations in concentrations of manganese are largely defined by changes in body weight, which in turn are dependent on the gametogenesis-spawning cycle. Sex was also a major factor influencing manganese concentrations in the mussel *Mytilus edulis*, with higher manganese concentrations in the gonads of females compared to males.

Ichikawa (1961) reported BCFs ranging from 80 in *Scomber* sp. to 50,000 in *Octopus vulgaris* collected from the coast of Japan. There was no evidence of strong biomagnification.

No reports on the bioconcentration of manganese in corals could be found. Metals can accumulate in coral tissues or skeletons, and corals may produce mucous to bind metals and regulate them.

Fish

Fish do not accumulate manganese to the same extent as organisms at lower trophic levels, with typical BCFs of about 100 (WHO, 2004). Ichikawa (1961) reported a BCF of 70 for *Pleuronectes* sp on the Japanese coast.

Manganese concentrations in the tropical barramundi (*Lates calcarifer*) collected from Lake Murray in Papua New Guinea in August 1988 ranged from 0.07-0.14 µg/g wet weight, with a mean of 0.095 µg/g. Several months later, the mean of 27 tissue samples was similar (0.054 µg/g) with a range of 0.027-0.096 µg/g (Currey et al., 1992). Manganese concentrations in barramundi were lower than those reported for other marine fish such as finfish (mean of 0.14 µg Mn/g wet weight) in New Zealand waters (Vlieg et al., 1991).

Summary

Manganese bioconcentration is common in most aquatic organisms, with marine organisms accumulating manganese more than freshwater species. Manganese has been shown to bioaccumulate to higher levels in plants and invertebrates, than in fish. Marine fish, invertebrates and plants concentrate manganese by factors of up to 100, 55,000 and 100,000 respectively. Typical concentrations of manganese in algae, seagrasses, coral and invertebrates range from 5-50 µg/g, while tissues from marine fish contain 0.1-10 µg/g.

There is no evidence that manganese biomagnifies, i.e. increases in concentration at higher trophic levels.

Mechanism of Manganese Toxicity

Studies on the mechanism of manganese toxicity have only been carried out on freshwater species at concentrations well above that found in even the most polluted sites. In algae, manganese can affect chlorophyll synthesis, while in fish, manganese disrupts carbohydrate metabolism, haematological parameters and sodium and calcium metabolism, ultimately leading to oxygen deprivation.

One study on the marine Norway lobster *Nephrops norvegicus* exposed to 20 mg Mn/L for 10 days, showed that the maturation of haemocytes and the number of haemocytes in the lobster was reduced due to increased apoptosis (programmed cell death). Reduced haemocytes is indicative of suppression of the immune system which may cause an increase in the prevalence of infections in the lobster (Hernroth et al., 2004, Oweson et al., 2006).

Toxicity of MnO_2 to Marine Biota

Manganese is one of the least toxic metals to marine biota, with toxicity depending on its chemical speciation. In general, colloidal and particulate forms of manganese, such as MnO_2 have low bioavailability, whereas dissolved Mn(II) and Mn(VII), and organically bound manganese, are only toxic at very high concentrations (Luoma, 1983).

The toxicity of manganese to marine biota was recently summarised in a comprehensive review by Stauber (2006). Most of the available data were on the toxicity of dissolved manganese (II). An additional search of the literature was carried out to determine if there was any further information on the toxicity of manganese oxides.

Very little additional information on the toxicity of manganese oxides was found, despite searching major on-line databases including the USEPA Ecotox database, CSA, CSIRO library database, Web of Science and Google Scholar. The limited data found are confounded by the fact that manganese oxides are insoluble at seawater pH, making it difficult to test the toxicity of manganese oxides to marine biota under laboratory conditions.

The material safety data sheet from Chemwatch for manganese tetroxide (Mn_3O_4) reported no acute toxicity to the copepod *Acartia tonsa* or to the marine alga *Skeletonema costatum* (EC50 of >10,000mg/L), but no further details or references were given.

The toxicity of Mn(IV), Mn(VII) and Mn(II) to hatching of brine shrimp (*Artemia salina*) cysts over a 48-h exposure was reported by Liu and Chen (1987). Concentrations of 100 mg/L of Mn(II), Mn(IV) and Mn(VII) caused 18%, 31% and 92% inhibition of hatching compared to controls, i.e. Mn(VII) was the most toxic, followed by Mn(IV) followed by Mn(II). However, manganese precipitated at concentrations of 10 mg/L and above (the lowest concentration tested) so it is not possible to determine whether dissolved manganese or the MnO_2 precipitate was responsible for the observed toxic effects for all manganese valence states. There was similar and low inhibition for all valence forms of manganese at 10 mg/L (12-16%). Neither total nor dissolved manganese concentrations were measured in the test solutions, so it is difficult to conclude whether there was really a difference in toxicity between manganese oxides and Mn(II). Such high manganese concentrations would rarely be encountered in marine systems, except possibly under hypoxic conditions in bottom waters which may occur for periods of several months. (Trefry et al., 1984).

The only other study that investigated the bioavailability of manganese from manganese dioxide was a freshwater study by Satoh et al. (1987). When carp were fed a diet supplemented with various forms of manganese, manganese bioavailability from manganese dioxide was low compared to manganese added as Mn(II). This study confirmed that manganese was essential in the diet of carp, otherwise growth rates were reduced and dwarfism was prevalent.

No published reports on the physical effects of manganese dioxide e.g. smothering or gill clogging could be found. However, research being undertaken at the Department of Marine Ecology, Goteborg University, Sweden, has shown that under conditions of hypoxia, dissolved manganese and iron are released from sediments and iron and manganese precipitate on the gills (as MnO_2 and iron oxyhydroxides) and exoskeleton of the Norway lobster (Baden et al, 1990). The effect of the precipitated layer has not yet been investigated but the authors hypothesised that it may hamper normal function of the gills, leading to internal hypoxia. As in mammalian cells, dissolved manganese can accumulate in the brain, blocking nerve calcium channels of the nerve synapses, which may affect food search behaviour in lobsters (Baden and Eriksson, 2006).

Effects of Manganese on Benthic Biota

Manganese is generally considered to be of low toxicity to sediment-dwelling organisms. For example, a sediment containing 345 mg Mn/kg, collected from a NSW port, was not acutely toxic to the estuarine amphipod *Corophium* sp. over a 10-day exposure (Stauber et al., 2000). Despite a concentration of 1.5 mg Mn(II)/L in filtered porewater, this sediment was not toxic to the benthic marine alga *Entomoneis* cf. *punctulata* in a whole sediment toxicity test (Stauber et al., 2000). This test measures the decrease in enzyme activity (esterase) in the alga over a 3-24-h exposure. Adams (2000) showed that there was no effect on enzyme activity in this alga at concentrations up to 2.5 mg Mn/L.

In contrast, Doyle (1999) found that manganese was strongly implicated as the cause of toxicity of pore water samples from Lake Macquarie, NSW. Total manganese concentrations in the pore waters ranged from 50-5272 µg/L, similar to the concentrations known to affect sea urchin larval development over 72 h (NOEC of 1.3 mg Mn/L and EC50 of 5.2 mg/L). When pore waters were spiked with additional manganese, toxicity was increased. However, the author suggested that manganese in these sediments was not due to anthropogenic inputs, but was present due to natural sources.

Bioavailability of Metals Adsorbed to MnO_2

Although manganese oxides appear to be of low toxicity to marine biota, their low solubility, large surface area and favourable surface charge at seawater pH make them efficient scavengers of other trace metals. While this will potentially lower metal availability to water column species, it may increase metal availability to benthic biota that ingest sediment particles. The availability of adsorbed metals will depend on their degree of association with manganese oxides and on the tendency of the metal complexes to re-adsorb. Enhanced metal bioavailability is likely in metal-rich environments and for those metals that have the greatest affinity for manganese oxides, such as Pb, Co, Ni, Cu, Zn and Ag.

Manganese oxide coatings and attached metals may be dissolved in the guts of sediment-dwelling organisms (e.g. tubificid worms), where pH and redox potential favour reducing conditions, rendering the metals available for uptake. Increased uptake of copper adsorbed to manganese dioxide in freshwater sediments has been observed (Diks and Allen., 1983). In contrast, Cooke et al. (1979) showed that cadmium on MnO_2 in sediments was not taken up by marine cockles in short-term exposures (96-h), presumably due to the strong adsorptive properties of the sediments.

Manganese oxides, and presumably metals adsorbed to them, appear to be more bioavailable than iron oxides because of the greater manganese-reducing tendency of gastrointestinal enzymes. In the clam (*Macoma balthica*), the transfer factor for radiolabelled silver from MnO_2 was 100 times faster than for silver bound to iron oxides (Luoma, 1989). Turner and Olsen (2000) showed that contaminants associated with manganese oxides in estuarine sediments were significantly more bioavailable than those associated with iron oxides in the guts of the teleost *Pleuronectes platessa* (plaice). Principal sources of Fe, Mn and Zn for this species are ingested food, rather than seawater or sediment. Reductive solubilisation of manganese oxides in their guts is faster at low pH because of greater adsorption of organic acids and dissolution of Mn(II). Ligands released from digested food and enzymes in gut fluid are important reductants of manganese via surface complexation reactions.

Beyer and Day (2004) found that lead bound to manganese and iron oxides from Chesapeake Bay was deposited on the surface of vegetation and then eaten by water fowl, providing an additional route of exposure to metals.

Remobilisation of Metals Adsorbed to MnO_2

Manganese oxides can scavenge dissolved metals at neutral pH under oxic conditions, thereby reducing the bioavailability of other metals. However, when MnO_2 is reduced, these metals can be released back into the water column, where they may or may not have an effect on biota before they are re-adsorbed.

Remobilisation of metals from manganese oxides in sediments back into the water column can occur with changes in salinity, redox potential, lowered pH or increase in complexing agents (Singh and Subramanian,1984). Such changing environmental conditions e.g. dredging, can transfer metals associated with MnO_2 in sediments into the aqueous phase (Samant et al., 1990; Cooke et al., 1979). Metals mostly associated with the manganese oxides are Pb, Co, Ni, Cu, Zn, Ag. These metals can be remobilised by moderately reducing conditions and then re-adsorption may occur (Koschinsky et al., 2001).

Amelioration of Metal Toxicity by Manganese

Manganese at low concentrations (4 µg/L) has been shown to ameliorate the toxicity of copper to the marine alga *Nitzschia closterium* (Stauber and Florence, 1985). In the presence of algae or bacteria, Mn(II) may be oxidised at the algal cell surface to Mn(III), probably by superoxide radicals. Manganese associated with the cells (as Mn(II) or Mn(III) hydroxides) adsorbs copper and prevents copper penetration into the cells. For *Nitzschia*, although there was competitive binding at the cell surface between copper and manganese, copper did not affect intracellular manganese concentrations. Manganese was also shown to be an effective scavenger of superoxide radicals produced in the chloroplast by the reduction of molecular oxygen. Manganese catalyses the dismutation of superoxide to H_2O_2 and O_2, providing further protection for the algal cell. Manganese was also shown to ameliorate copper toxicity to diatoms in a laboratory microcosm experiment (Beck et al., 2002).

Manganese oxides are also a major component of biofilms and periphyton and adsorb metals (Gray et al., 1987). Aquatic consumers of periphyton may receive a lower exposure from manganese oxide adsorbed metals compared to organically adsorbed metals (Newman and McIntosh, 1989).

Manganese oxide sheaths on bacteria, when fed to the marine mussel *Mytilis trossulus,* decreased the concentration of lead and cadmium in the mussel tissue by increasing metal clearance rates (Widmeyer et al., 2004).

Conclusions

- Literature data suggest that manganese bioconcentration is common in most aquatic organisms, and is higher in plants and invertebrates than in fish. Marine fish, invertebrates and plants concentrate manganese by factors of up to 100, 55,000 and 100,000 respectively. There is no evidence that manganese biomagnifies, i.e. increases in concentration at higher trophic levels.
- Only limited data on the direct toxicity of MnO_2 were found. It is generally believed that manganese in colloidal or particulate forms (as MnO_2) is less toxic than soluble Mn(II).
- Indirect effects of MnO_2 on marine biota are variable. Manganese oxides can scavenge dissolved metals at neutral pH under oxic conditions, thereby reducing the bioavailability of other metals to marine algae, periphyton and mussels via water exposures. In contrast, metals adsorbed to MnO_2 in sediments may be bioavailable in the guts of sediment-dwelling species that ingest sediments.
- No published reports on the physical effects of manganese e.g. smothering or gill clogging could be found. Manganese precipitation on the gills and exoskeletons of the Norway lobster has been observed, but it is not yet known whether this causes internal hypoxia in the lobster.

References

Adams, M.S. (2000). Development of a whole sediment toxicity test using a benthic microalgae. B.Sc (Hons) Thesis, University of Technology, Sydney, 99 pp.

ANZECC/ARMCANZ (2000). Australian and New Zealand Guidelines for Fresh and Marine Water Quality. National Water Quality Management Strategy, Australian and New

Zealand Environment Conservation Council and Agriculture and Resource Management Council of Australia and New Zealand.

Apte, S.C. (2006). Manganese(II) oxidation rates in seawater. CSIRO Land and Water Report, 4 pp.

Baden, S.P. and Eriksson, S.P.(2006). Role, routes and effects of manganese in crustaceans. *Oceanography and Marine Biology: An Annual Review* 44, 61-83.

Baden, S.P., Pihl, L. and Rosenberg, R. (1990). Effects of oxygen depletion on the ecology, blood physiology and fishery of the Norway lobster, *Nephrops norvegicus*. Marine Ecology Progress Series 67, 141-155.

Beck, N.G., Bruland, K.W. and Rue, E.L. (2002). Short term biogeochemical influence of a diatom bloom on the nutrient and trace metal concentrations in South San Francisco Bay microcosm experiments. *Estuaries* 25, 1063-1076.

Beyer, W.N. and Day, D. (2004). Role of manganese oxides in the exposure of mute swans (*Cygnus olor*) to lead and other elements in the Chesapeake Bay, USA. Environmental pollution 129, 229-235.

Boyden, C.R. and Phillips, D.J.H. (1981). Seasonal variation and inherent variability of trace elements in oysters and their implications for indicator studies, *Marine Ecology Progress Series* 5, 29-40.

Brinkhuis, B.H., Penello, W.F. and Churchill, A.C. (1980). Cadmium and manganese flux in eelgrass *Zostera marina* II. Metal uptake by leaf and root-rhizome tissues. *Marine Biology* 58, 187-196.

Cooke, M., Nickless, G., Lawn, R.E. and Roberts, D.J. (1979). Biological availability od sediment-bound cadmium to the edible cockle *Cerastoderma edule*. *Bulletin of Environmental Contamination and Toxicology* 23, 381-386.

Currey, N.A., Benko, W.I., Yaru, B.T. and Kabi, R. (1992). Determination of heavy metals, arsenic and selenium in barramundi (*Lates calcarifer*) from Lake Murray, Papua New Guinea. *The Science of the Total Environment* 125, 305-320.

De Laune, R.D., Reddy, C.N. and Patrick, W.H.Jr. (1981). Accumulation of plant nutrients and heavy metals through sedimentation processes and accretion in a Lousiana salt marsh, *Estuaries* 4, 328-334.

Diks, D.M. and Allen, H.E. (1983). Correlation of copper distribution in a freshwater-sediment system to bioavailability. *Bulletin of Environmental Contamination and Toxicology* 30, 37-43.

Doyle, C. (1999). Toxicity characterisation of contaminated sediment pore water using the sea urchin *Heliocidaris tuberculata*. B.Sc (Environmental Biology) Honours Thesis, University of Technology, Sydney, 106 pp.

Goldberg, E.D., Broecker, W.S., Gross, M.G. and Turckian, K.K. (1971). Marine chemistry. In Radioactivity in the Marine Environment. National Research Council Panel on Radioactivity in the Marine Environment, National Academy of Sciences, Washington, D.C., 137-146.

Grey, B.R., Hill, W.R. and Stewart, A.J. (2001). Effects of development time, biomass and ferromanganese oxides on nickel sorption by stream periphyton. *Environmental Pollution* 112, 1-71.

Hansen, S. N. and Bjerregaard, P. (1995). Manganese kinetics in the sea star *Asterias rubens* (L.) exposed via food or water. *Marine Pollution Bulletin* 31, 127-132.

Hernroth, B., Baden, S.P., Holm, K.,Andre, T. and Soderhall, I. (2004). Manganese induced immune suppression of the lobster *Nephrops norvegicus. Aquatic Toxicology* 70, 223-231.

Huntsman, S.A. and Sunda, W.G. (1980). The role of trace metals in regulating phytoplankton growth with emphasis on Fe, Mn and Cu. In: Studies in Ecology 1; The Physiological Ecology of Phytoplankton, I. Morris (ed), University of California Press, 285-328.

Ichikawa, R. (1961). On the concentration factors of some important radionuclides in marine food organisms. *Bulletin of the Japanese Society of Scientific Fisheries* 27, 66-74.

Ikuta, K. and Nakahara, M. (1987). Distributions of 54-Mn and stable-Mn in tissues of female and male of a whelk *Volutharpa ampullacea perryi*. *Nippon Suisan Gakkaishi* 53, 809-812.

Khristoforva, N.K. and Bogdanova, N.N. (1981). Environmental conditions and heavy metal content of marine organisms from atolls of the Pacific Ocean. Proceedings of the Fourth International Coral Reef Symposium, Manila 1, 161-162.

Koschinsky, A., Fritsche, U. and Winkler, A. (2001). Sequential leaching of Peru Basin surface sediment for the assessment of aged and fresh heavy metal associations and mobility. *Deep-Sea Research* 48, 3683-3699.

Liu, P-C. and Chen, J-C. (1987). Effects of heavy metals on the hatching rates of brine shrimp *Artemia salina* cysts. *Journal of the World Aquaculture Society* 18, 78-83.

Luoma, S.N. (1989) Can we determine the biological availability of sediment-bound trace elements? *Hydrobiologia* 176/177, 379-396.

Newman, M.C. and McIntosh, A.W. (1982). The influence of lead in components of a freshwater ecosystem on molluscan tissue lead concentrations. *Aquatic Toxicology* 2, 1-19.

Norstedt, M. (2004). Uptake of manganese through experimental feeding in Norway lobster *Nephrops norvegicus*. MSc thesis, Department of Marine Ecology, Goteborg University, Sweden.

Nye, L.B. (1990). Trace metal accumulation under differing sediment conditions in the magrove, *Rhizophora mangle* L., from Key Largo, Florida. M.S. thesis. University of Miami, Coral Gables, FL, USA.

Oweson, C.A.M., Baden, S.P. and Hernroth, B.E. (2006). Manganese induced apoptosis in haemopoietic cells of Nephrops norvegicus (L.) *Aquatic Toxicology*, 77, 322-328.

Peters, E.C., Gassman, N.J., Firman, J.C., Richmond, R.H. and Power, E.A. (1997). Ecotoxicology of tropical marine ecosystems. *Environmental Toxicology and Chemistry* 16, 12-40.

Samant, H.S., Doe, K.G. and Vaidya, O.C. (1990). An integrated chemical and biological study of the bioavailability of metals in sediments from two contaminated harbours in New Brunswick, Canada. *The Science of the Total Environment*, 96, 253- 268.

Satoh, S., Takeuchi, T. and Watanabe, T. (1987). Availability to carp of manganese in white fish meal and of various manganese compounds. *Nippon Suisan Gakkaishi* 53, 825-832.

Singh, S.K. and Subramanian, V. (1984). Hydrous Fe and Mn oxides – scavengers of heavy metals in the aquatic environment. *Critical Reviews in Environmental Control*, 14, 33-90.

Stauber, J.L. (2006). Derivation of a manganese trigger value for Port Curtis. CSIRO Land and Water Science Report 45/06, 14 pp.

Stauber, J.L. and Florence, T.M. (1985). Interactions of copper and manganese: a mechanism by which manganese alleviates copper toxicity to the marine diatom, *Nitzschia closterium* (Ehrenberg) W. Smith. *Aquatic Toxicology* 7, 241-254.

Stauber, J.L., Brockbank, C.I., Adams, M.S. and Binet, M.T. (2000). Ecotoxicological testing of dredged sediment in Newcastle Harbour. CSIRO Energy Technology Investigation Report No ET/IR212R, 15 pp.

Stokes, P.M., Campbell, P.G.C., Schroeder, W.H., Trick, C., France, R.L., Puckett, K.J., Lazerte, B., Speyer, M., Hanna, J.E. and Donaldson, J. (1988). Manganese in the Canadian Environment. National Research Council of Canada NRCC Associate Committee on Scientific Criteria for Environmental Quality, 177 pp.

Sunda, W.G. and Kieber, D.J. (1994). Oxidation of humic subtances by manganese oxides yields low molecular-weight organic substrates. Nature 367, 62-64.

Trefy, J.H., Presley, B.J., Keeney-Kennicutt, W.L., Troocine, R.P. (1984). Distribution and chemistry of manganese, iron and suspended particulates in Orca Basin. *Geo-Marine Letters* 4, 125-130.

Turner, A. and Olsen, Y.S. (2000). Chemical versus enzymatic digestion of contaminated estuarine sediment: relative importance of iron and manganese oxides in controlling trace metal bioavailability. *Estuarine, Coastal and Shelf Science* 51, 717-728.

Vlieg, P., Lee, J. and Grace N.D. (1991). Elemental concentration of marine and freshwater finfish, and shellfish from New Zealand waters. *Journal of Food Composition and Analysis* 4, 136-147.

WHO (2004). Manganese and its compounds: environmental aspects. Concise International Chemical Assessment Document 63, International Program on Chemical Safety, World Health Organization, Geneva.

Widmeyer, J.R., Crozier, E.D., Moore, M.M., Jurgensen, A. and Bendell-Young, L.I. (2004). Role of Leptothrix discophora in mediating metal uptake in the filter-feeding bivalve *Mytilus trossulus* (*edulis*). Environmental Science and technology 38, 769-774.

WSC/NSR (1995). Review of the effects of manganese on aquatic life and human health. Water Studies Centre, Monash University and NSR Environmental Consultants, 36 pp

Appendix B6- Derivation of a Manganese Trigger Value for Port Curtis, Queensland

Derivation of a Manganese Trigger Value for Port Curtis, Queensland

J.L. Stauber
CSIRO Land and Water Science Report 45/06
October 2006

Prepared for URS

Commercial-in-confidence

Enquiries should be addressed to:

Dr Jenny Stauber

61 2 9710 6808 or 852 23581399

Jenny.Stauber@csiro.au

Distribution list

Jenny Stauber	1
Peter Collins	1
Land and Water Library	3 (1 e-copy, 2 hard)
	1

Important Notice

Executive Summary

Gladstone Pacific Nickel Ltd (GPNL) is currently investigating the feasibility of developing a high pressure acid leach refinery to produce nickel and cobalt in the Yarwun Precinct of Gladstone, Queensland. The development will include a waste liquor-seawater discharge into Port Curtis. Preliminary test work and modelling has shown that the wastewater will contain manganese and, due to poor tidal flushing in Port Curtis, concentrations of manganese may be above the current ANZECC/ARMCANZ (2000) guideline (80 µg/L). Habitats of concern in Port Curtis include mangroves and seagrasses (home of protected dugongs), principally along the southwestern shoreline, with corals more common on the eastern side of the Bay.

The current manganese trigger value (ANZECC/ARMCANZ, 2000) is a low reliability guideline, based on limited temperate data from overseas. The objective of this desk study was to collect additional information on the toxicity of manganese to marine biota and to use this data to re-derive a more defensible manganese guideline, appropriate to the marine ecosystems of Port Curtis.

The effects of manganese on marine biota are not well documented, with little data available for tropical species. However, limited data suggest that manganese is one of the least toxic metals to marine biota. Reported LC/EC50 values range from 1.5-50 mg/L for algae, 5-40 mg/L for molluscs and echinoderms, and 50-70 mg/L for adult crustacea. Acute and chronic effects on marine organisms are generally only detectable at concentrations of manganese above 5 mg/L, usually well in excess of environmental manganese concentrations. Exceptions include two marine microalgae, one coral and early life stages of one marine crab, where effects down to 0.5 mg Mn/L have been noted.

Quality-checked literature data on manganese toxicity to marine biota from ANZECC/ARMCANZ (2000) and WHO (2004) were combined with data from tests with six Australian species, including one coral, and used in species sensitivity distributions (SSDs) according to the ANZECC/ARMCANZ approach. Trigger values for manganese to protect 95% of species with 50% confidence, suitable for slightly-moderately disturbed ecosystems, ranged from 140 – 340 µg Mn/L, depending on the choice of data and the choice of acute to chronic ratios (ACR).

The most appropriate and conservative manganese trigger value for Port Curtis was based on the use of the experimentally derived ACR, using all the combined data (literature values and local species). For the areas in Port Curtis where corals are of concern, e.g. on the eastern side of the Harbour, a manganese trigger value of 140 µg/L is a best estimate. It should be noted however, that data for only one coral at Heron Island, was used in the SSD.

No data were available on the toxicity of manganese to seagrasses and mangroves, so it is not known whether these species are more sensitive to manganese than algae and invertebrates. There are insufficient data in the literature to determine whether tropical species are likely to be more sensitive than temperate species to manganese. For this reason, and because tidal flushing in Port Curtis is poor, a conservative TV of 140 µg Mn/L is recommended for Port Curtis overall. This can be a considered to be a moderate reliability guideline and is about two-fold higher than the current low reliability TV for manganese of 80 µg/L (ANZECC/ARMCANZ, 2000).

This trigger value is based on Mn(II). Additional work will be required to determine whether oxidation of manganese occurs post discharge, and whether a manganese precipitate may cause smothering or other effects on benthic biota in sediments. Toxicity testing using local tropical species, particularly mangrove inhabitants such as crabs, together with corals and seagrasses (for which few tests are currently available) is also desirable, to further reduce uncertainties associated with the proposed manganese trigger value.

Table of Contents

Executive Summary 3
Introduction 5
Results and Discussion 5
Toxicity of manganese to marine biota 5
Water quality guidelines for manganese 6
Conclusions 12
References 113

List of Tables

Table 1. Summary of manganese toxicity data from WHO(2004) 7
Table 2. Toxicity of manganese to Australian species 8
Table 3. Manganese Trigger Values Estimated Using the Combined Data Sets 12

Table of Figures

Figure 1. WHO (2004) SSD 7
Figure 2. SSD derived from the local toxicity tests (no coral) 9
Figure 3. SSD derived from the local toxicity tests (including coral. 9
Figure 4. Acute and chronic data (n=14, no coral data) combined as outlined in 1. 10
Figure 5. Acute and chronic data (n=15, including coral data) combined as outlined in 2… 11
Figure 6. Acute and chronic data (n=14, no coral data) combined as outlined in 3…… ..11
Figure 7. Acute and chronic data (n=15, including coral data) combined as outlined in 4…..12

Introduction

Gladstone Pacific Nickel Ltd (GPNL) is currently investigating the feasibility of developing a high-pressure acid-leach refinery to produce nickel and cobalt in the Yarwun Precinct of Gladstone, Queensland. The site is bounded by Reid Rd to the west and the Calliope River, which flows into Port Curtis to the east.

A slurry pipeline will transport ore slurry from the nearby Marlborough mine to the Yarwun refinery. Neutralised residue from the Yarwun refinery will be stored in a residue storage facility in the Adolga area, close to Comalco's existing residue management area. After residue dewatering, the liquor will either be reused or surplus liquor combined with seawater cooling water and discharged via a diffuser to Port Curtis.

Preliminary test work and modelling has shown that the wastewater will contain manganese and, due to poor tidal flushing in Port Curtis, concentrations of manganese may be above the current ANZECC/ARMCANZ (2000) guideline (80 µg/L). Habitats of concern in Port Curtis include mangroves and seagrasses (home of protected dugongs), principally along the southwestern shoreline, with corals more common on the eastern side of the Bay.

The current manganese trigger value (ANZECC/ARMCANZ, 2000) is a low reliability guideline, based on limited temperate data from overseas. An application factor of 200 was applied to the most sensitive species (a mollusc) to derive a trigger value of 80 µg/L. The objective of this desk study was to collect additional information on the toxicity of manganese to marine biota and to use this data to re-derive a more defensible manganese guideline, appropriate to marine ecosystems of Port Curtis.

Results and Discussion

Toxicity of Manganese to Marine Biota

The effects of manganese on marine biota are not well documented, with little data available for tropical species. However, limited data suggest that manganese is one of the least toxic metals to marine biota. Reported LC/EC50 values range from 1.5-50 mg/L for algae, 5-40 mg/L for molluscs and echinoderms, and 50-70 mg/L for adult crustacea. Crab embryos and corals appear to be the most sensitive species to manganese (see below).

Manganese showed low toxicity to the marine diatoms *Ditylum brightwellii*, and *Asterionella japonica*, with EC50 values of 1.5 mg/L and 4.9 mg/L respectively (Canterford and Canterford, 1980; Fisher and Jones, 1981). The diatom *Phaeodactylum tricornutum* was less sensitive, with a 96-h EC50 (growth rate) of 37 mg/L (ANZECC/ARMCANZ, 2000).

Molluscs and echinoderms are insensitive to manganese at environmentally relevant concentrations. Manganese had no effect on the settlement success of the oyster *Crassostrea gigas* and larval behaviour was not affected at concentrations of up to 20 µg/L (Watling 1983). Young and Nelson (1974) also found no effect on the motility of sea urchin sperm at 0.14 mg/L. Sperm motility was only slightly affected at concentrations of 0.68 mg Mn/L.

.

With the exception of crab embryos, crustaceans have been reported to be insensitive to manganese. Liu and Chen (1987) determined the effect of three manganese oxidation states on the relative hatching percentage of cysts of the brine shrimp *Artemia salina* after 48-h exposure at 28^{o}C. Concentrations of 100 mg/L of Mn(II), Mn(IV) and Mn(VII) gave 82%, 69% and 8% of control respectively. However, results were confounded by the precipitation of Mn(IV) at concentrations in excess of 10 mg/L.

In contrast, embryos of the brachyuran crab *Cancer anthonyi*, were sensitive to manganese (Macdonald et al., 1988). Because this species broods embryos externally on the abdomen, the embryos are exposed to contaminants in waters and sediments continuously. Concentrations of >100 mg/L gave 100% mortality of crab embryos over 7 days. Concentrations of 0.01-10 mg/L gave 27-45% mortality, however the response was not concentration-dependent. Hatching of embryos was also decreased at manganese concentrations of 0.01-10 mg/L, compared to controls. Eggs of the crab *Carcinus maenas* accumulate manganese (and other metals) during ovogenesis and when the eggs are extruded manganese also adsorbs to the chitinous vitelline membrane (Martin, 1976). This bioconcentration of manganese may explain why crab embryos are killed and larval hatching is impaired at lower manganese concentrations compared to other invertebrates.

Manganese has recently been reported to be toxic to the common coral *Stylophora pistillata,* reducing survival over 48 h and causing an unusual physiological response involving the disconnection or 'sloughing' of the coral tissue from the skeleton (Stauber et al., 2002). A concentration of manganese of 1.5 mg/L caused 50% mortality (LC50) of adult coral colonies over a 48-h exposure, with no effect at 1.1 mg/L. Tissue sloughing was observed at lower concentrations, with a 48-h EC50 of 0.86 mg Mn/L and no effect at 0.51 mg Mn/L. Toxicity was associated with effects on the animal (host) fraction of the coral-algal symbiosis, rather than on the algal symbionts themselves. The disconnection of the coral tissue from the skeleton was an unusual response, with few reports of similar effects in the published scientific literature.

In summary, acute and chronic effects on marine organisms are generally only detectable at concentrations of manganese above 5 mg/L, usually well in excess of environmental manganese concentrations. Exceptions include two marine microalgae, one coral and early life stages of one marine crab. There is generally little overlap between background concentrations of manganese in seawater (<0.01 mg/L) and concentrations that cause effects in aquatic organisms.

Water Quality Guidelines for Manganese

ANZECC/ARMCANZ(2000)

ANZECC/ARMCANZ (2000) includes only a low reliability trigger value for manganese in marine waters. Marine data for 4 species from 3 taxonomic groups, were available including:

- 1 species of crustacean, with a 7-day LOEC for mortality of 70 mg/L
- 1 species of mollusc, with a 48-h EC50 of 16 mg/L
- 2 species of algae, one (*Phaeodactylum tricornutum*) with a 96-h EC50 for growth ranging from 25.7-53.8 mg/L (mean 37.2), and the other (photosynthesis endpoint) not used.

The lowest value was for the mollusc (16 mg/L) and this was divided by an assessment factor of 200 (for an essential metal) to give a low reliability trigger value of 0.08 mg/L.

This trigger value appears to be conservative given that an extensive review of the literature by Stauber and Binet (2001) showed that algae and invertebrates had LC/EC50 values ranging from 1.5-70 mg Mn/L.

WHO (2004) Data

The available literature-based toxicity data for manganese in marine waters (pre-screened for data quality) was sourced from the draft WHO Concise Information Chemical Assessment Document for Manganese (WHO, 2004), and is summarised in Table 1. NOEC values were

not reported for any of the tests included in Table 1, therefore LC50 acute values were divided by an overall acute to chronic ratio of 10 and chronic/sub-chronic EC50 values were divided by 5, to give chronic NOEC values for use in the species sensitivity distribution (SSD).

Table1. Summary of manganese toxicity data from WHO(2004)

Organism	Duration	Type	EC_{50}/LC_{50} (mg/L)	Calculated Chronic NOEC (mg/L)
Ditylum brightwellii (diatom)	120 h	Chronic	1.5	0.3
Asterionella japonica	72 h	Chronic	4.9	1
Nitzschia closterium	96 h	Chronic	26	5.1
Nitocra spinipes (copepod)	96 h	Acute	70	7
Crassostrea virginica (oyster)	48 h	Acute	16	1.6
Mytilus edulis (mussel)	48 h	Sub-chronic	30	6
Cancer anthonyi (crab)[a]	168 h	Chronic	0.01 (LOEC)	-
Mya arenia (clam)	168 h	Acute	300	30
Artemia salina (brine shrimp)	48 h	Acute	52	5.2
Heliocidaris tuberculata (sea urchin)	72 h	Sub-chronic	5.2	1

[a]The *Cancer anthonyi* test had an unusually low lowest observed effect concentration (LOEC), and as noted earlier, there was no concentration dependence to the response in that test over a concentration range of 0.01 to 10 mg/L manganese. Because of this uncertainly, this test was not included in the WHO guideline derivation.

The calculated HC5(50) i.e. the hazardous concentration to protect 95% of species with 50% confidence was 0.3 mg Mn/L (Figure 1, WHO, 2004).

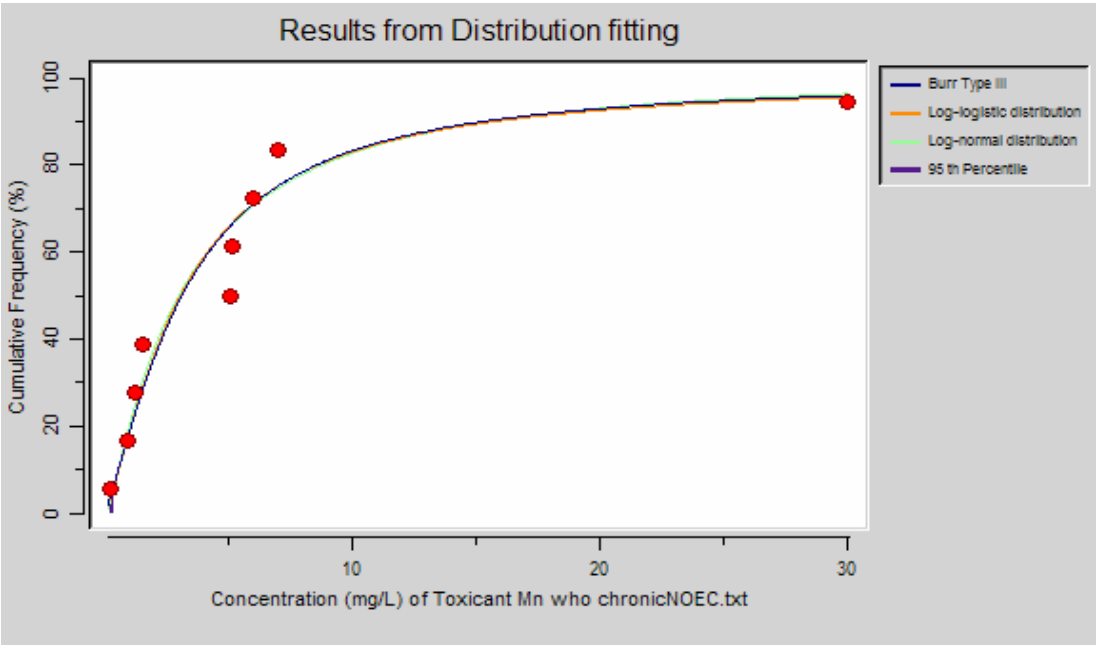


Figure 1. WHO (2004) species sensitivity distribution

Note that this SSD did not include fish data, and the data appear to be from more than one probability distribution, as evidenced by the two groups of derived NOEC values clustered above and below 5 mg/L Mn.

Manganese toxicity to Australian species

The toxicity of manganese to several Australian species was reported in Levy et. al. (2004). The following tests were used:

1. 60-h[1] larval abnormality test (sub-chronic) using the rock oyster *Saccostrea comercialis* (based on APHA method 8610C, modified for use with *S. commercialis* by Krassoi, 1996). A second, lethal (acute) endpoint (larval mortality) was also measured.
2. 72-h larval abnormality test (sub-chronic) using the sea urchin *Heliocidaris tuberculata* (based on APHA (1998) and Simon and Laginestra (1996)). A second, lethal (acute) endpoint was also measured.
3. 72-h algal growth rate inhibition (chronic) test using the marine diatom *Nitzschia closterium* (based on the protocol of Stauber et al., 1994).
4. 96-h acute toxicity test using the tropical juvenile tiger prawn *Penaeus monodon* (based on USEPA OPPTS 850.1045 and USEPA 1993 for mysid shrimp).
5. 96-h acute imbalance test using larvae of the Australian bass, *Macquaria novemaculeata.*

For all tests, manganese chloride solutions in filtered seawater were used as the test toxicant and results were expressed on the basis of measured manganese concentrations. The results of the tests are summarised in Table 2.

Table 2. Toxicity of manganese to Australian species (from Levy et al., 2004 and Stauber et al., 2002)

Species/duration	Endpoint	Type	NOEC(mg/L)	EC_{50}/LC_{50} (mg/L)
Rock oyster 60 h	Larval survival	Acute	3.1	10.8
	Larval abnormality	Sub-chronic	1.0	2.7
Sea urchin 72 h	Larval survival	Acute	3.1	14.3
	Larval abnormality	Sub-chronic	1.0	4.2
Tiger prawn 96 h	Survival	Acute	9	26.1
Larval bass 96 h	Imbalance	Acute	49	97.5
Microalga *Nitzschia* 72 h	Growth rate	Chronic	18	87
Coral *Stylophora pistillata* 48 h	Mortality	Acute	1.1	1.5

Acute and chronic tests with the oyster and sea urchin gave acute to chronic ratios (ACR), i.e. acute EC50/chronic NOEC of 10.8 and 14.3 respectively. The geometric mean ACR was 12.4 and this ACR was used in the SSD according to ANZECC/ARMCANZ (2000).

When coral data were excluded from the SSD, the PC(95)50 i.e. the concentration of manganese to protect 95% of species with 50% confidence was 680 µg/L (Figure 2). Inclusion of the sensitive coral data lowered the PC95(50) to 110 µg Mn/L (Figure 3). Curve fits were reasonable considering the small number of local species data available.

[1] This test is nominally conducted over a 48-h period, but in this case was extended to 60 h due to seasonal effects on larval development rates for this species.

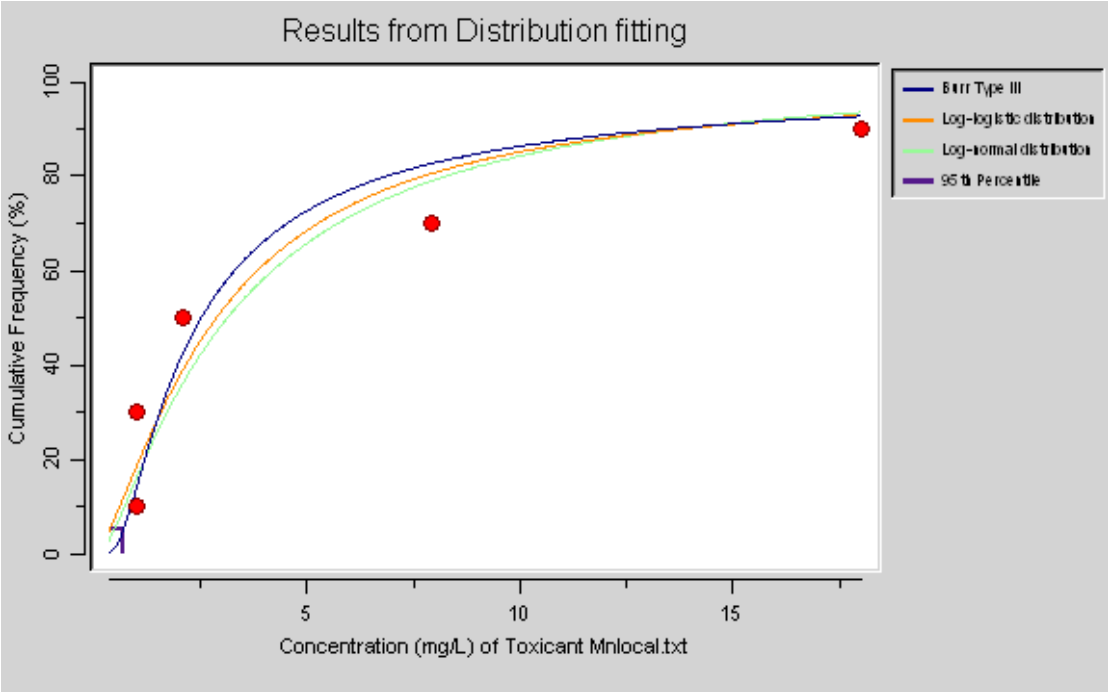
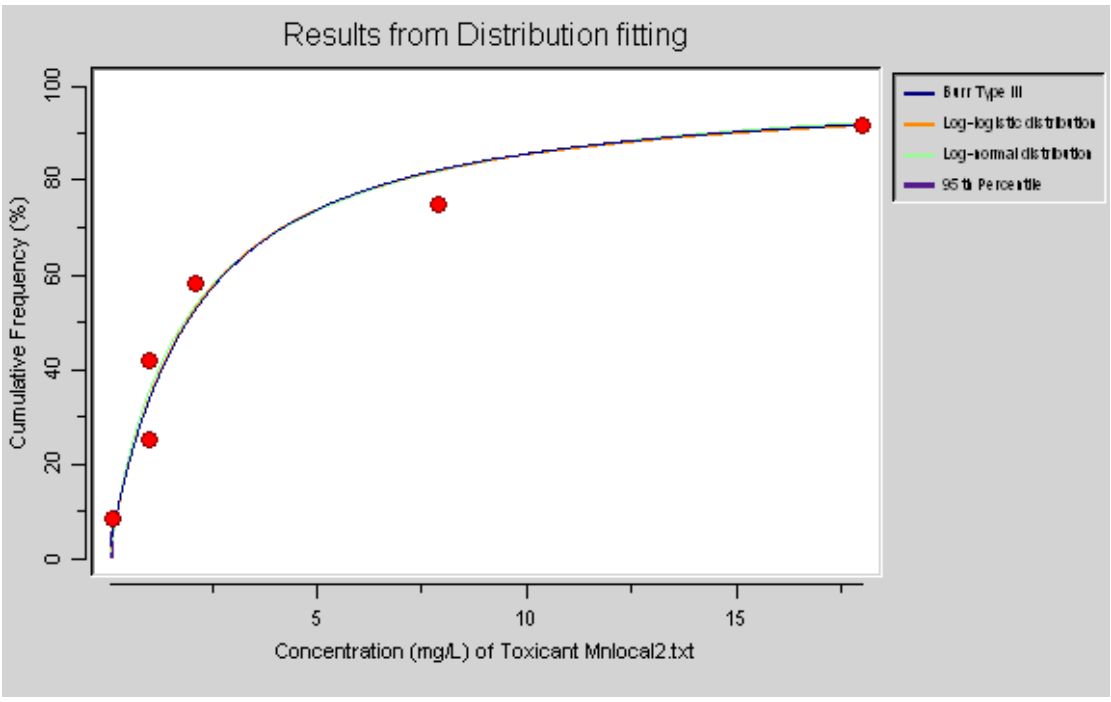


Figure 2. SSD derived from the local toxicity tests (no coral)



..

Figure 3. SSD derived from the local toxicity tests (including coral)

Combining all data

ANZECC/ARMCANZ (2000) provides little guidance on how best to combine acute and chronic data to generate trigger values using SSDs. SSDs were run using the BurrliOZ software (ANZECC/ARMCANZ, 2000) using the following combined data:

1. Eight acute and chronic data from WHO (2004), excluding the crab data, were used, together with one additional 96-h EC50 for the microalga *Phaeodactylum tricornutum* (ANZECC/ARMCANZ,2000) and local Australian data (5 species, excluding coral). Data for the sea urchin were used only once. The acute WHO EC/LC50 values were

first converted to chronic values using an ACR of 10 (factor 2 for an essential metal and factor 5 to convert to chronic NOEC equivalent). The chronic EC50 WHO and ANZECC/ARMCANZ data were converted to chronic NOEC values by dividing by 5 (ANZECC/ARMCANZ, 2000). For the local Australian data, chronic NOEC data were preferred and used without adjustment, while acute data (LC50 for prawns and bass), were converted to chronic NOEC data by dividing by an ACR of 10.

2. Data were used as above, except that the coral data were also included (acute LC50 divided by an ACR of 10).
3. Data used as in 1, except that an experimentally derived ACR of 12.4 was used instead of an ACR of 10 and applied to all acute data.
4. As for 3, except that coral data divided by an ACR of 12.4 was also included.

The resulting SSDs are shown in Figures 4-7 and the manganese trigger values are summarised in Table 3.

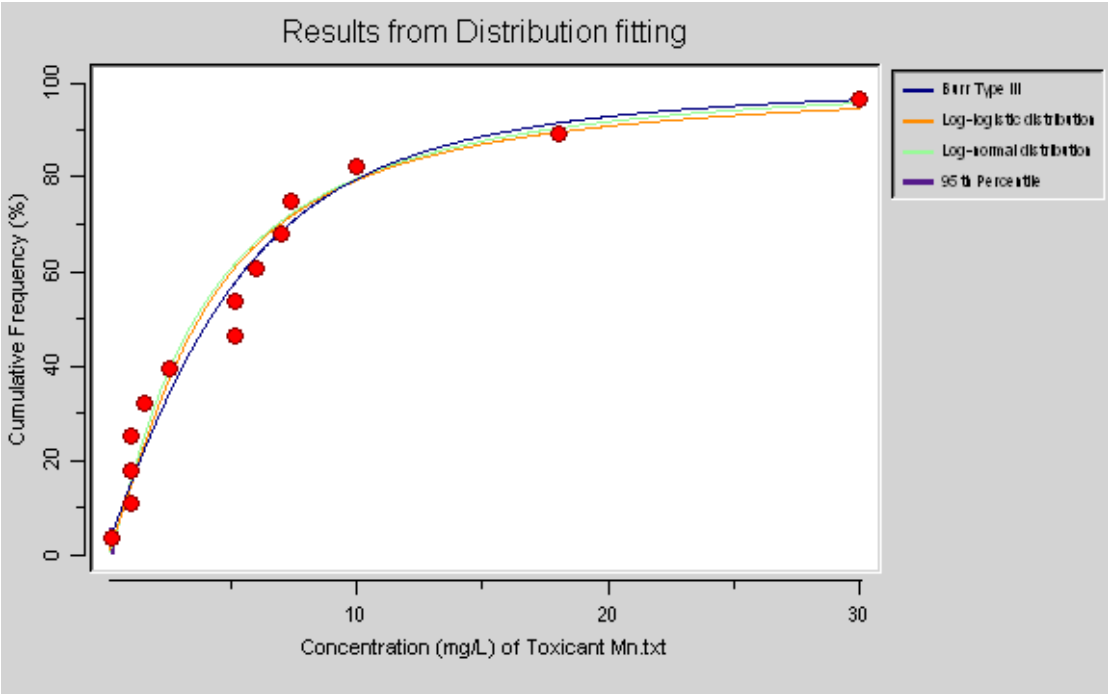


Figure 4. Acute and chronic data (n=14, no coral data) combined as outlined in 1. ACR=10**.**

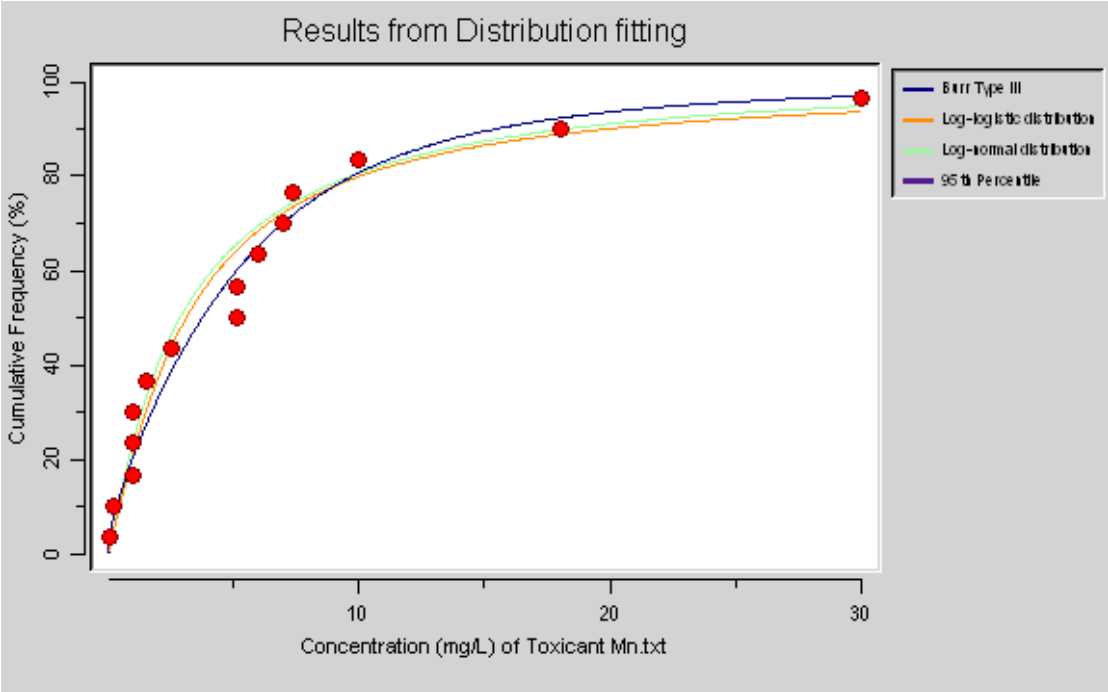


Figure 5. Acute and chronic data (n=15, including coral data) combined as outlined in 2. ACR=10.

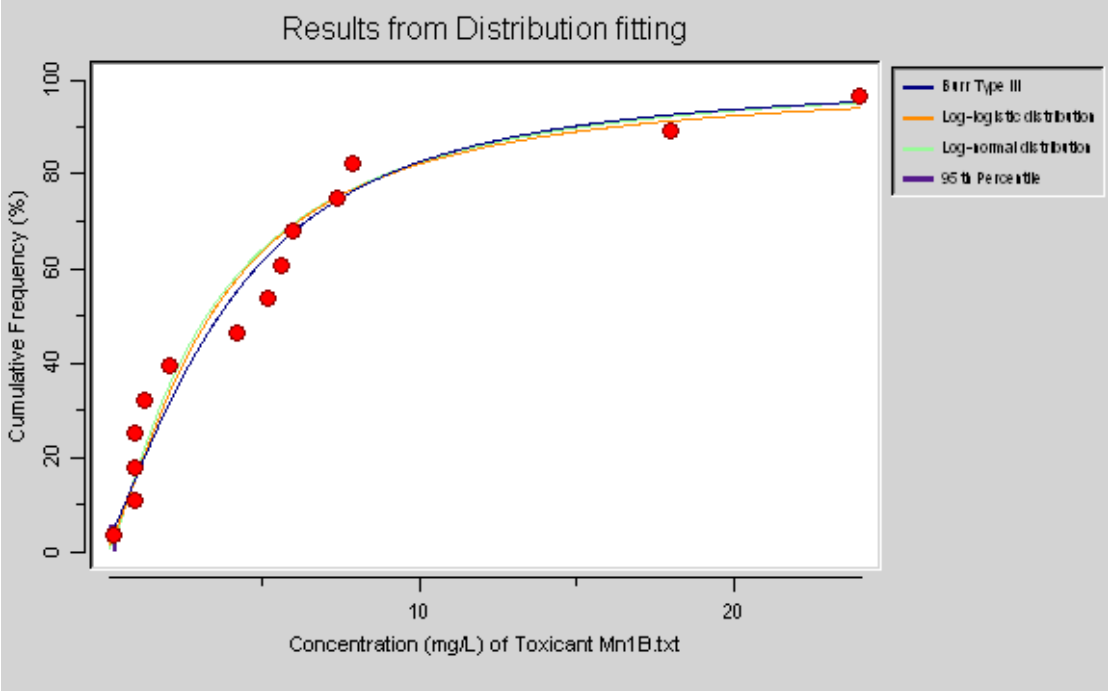


Figure 6. Acute and chronic data (n=14, no coral data) combined as outlined in 3. ACR=12.4 (experimentally derived).

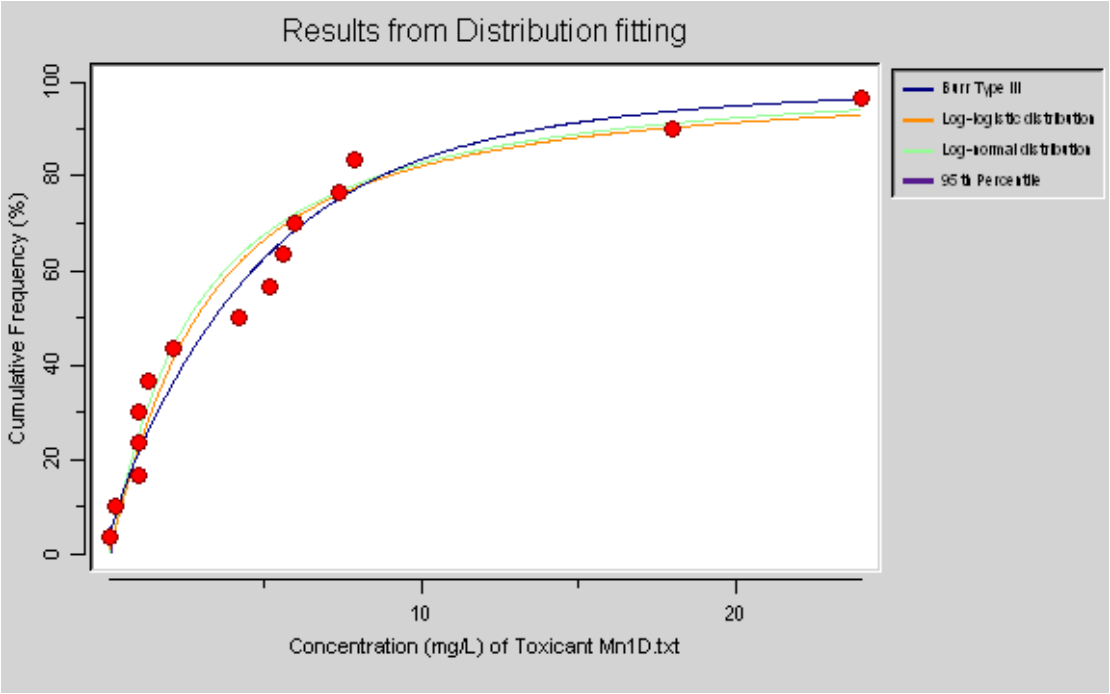


Figure 7. Acute and chronic data (n=15, including coral data) combined as outlined in 4. ACR=12.4 (experimentally derived).

Table 3. Manganese Trigger Values Estimated Using the Combined Data Sets

Data Set	ACR	Mn Trigger Value (µg Mn/L)
1. Excluding Coral	10	320
2. Including Coral	10	150
3. Excluding Coral	12.4	340
4. Including Coral	12.4	140

Conclusions

The most appropriate and conservative manganese trigger values for Port Curtis would be those based on the use of the experimentally derived ACR, using all the combined data (literature values and local species). For the areas in Port Curtis where corals are of concern, for example the eastern side of the Harbour, a manganese trigger value of140 µg/L is a best estimate. It should be noted however, that data for only one coral at Heron Island, was used in the SSD.

No data on the toxicity of manganese to seagrasses and mangroves were available, so it is not known whether these species are more sensitive to manganese than algae and invertebrates. There is insufficient data in the literature to determine whether tropical species are likely to be more sensitive than temperate species to manganese. For this reason, and because tidal flushing in Port Curtis is poor, a conservative TV of 140 µg Mn/L is recommended for Port Curtis overall. This can be a considered to be moderate reliability guideline and is about two-fold higher than the current low reliability TV for manganese (ANZECC/ARMCANZ, 2000).

This trigger value is based on Mn(II). Additional work will be required to determine whether oxidation of manganese occurs post discharge, and whether a manganese precipitate may cause smothering or other effects on benthic biota in sediments. Toxicity testing using local

tropical species, particularly mangrove inhabitants such as crabs, together with corals and seagrasses (for which few tests are currently available) is also desirable, to further reduce uncertainties associated with the proposed manganese trigger value.

References

Aldenberg, T. and Slob, W. (1993). Confidence limits for hazardous concentrations based on logistically distributed NOEC toxicity data. *Ecotoxicological and Environmental Safety* 25, 48-63.

ANZECC/ARMCANZ (2000) Australian and New Zealand Guidelines for Fresh and Marine Water Quality. National Water Quality Management Strategy, Australian and New Zealand Environment Conservation Council and Agriculture and Resource Management Council of Australia and New Zealand.

Canterford, G.S. and Canterford, D.R. (1980) Toxicity of heavy metals to the marine diatom *Ditylum brightwelli* (west) Grunow: Correlation between toxicity and metal speciation. *Journal of the Marine Biological Association of U.K.* 60, 227-242.

Fisher, N.S. and Jones, G.J. (1981) Heavy metals and marine phytoplankton: Correlation of toxicity and sulfhydryl-binding. *Journal of Phycology* 17, 108-111.

Krassoi R (1996). Adaptation of the 48h larval abnormality test using doughboy scallop and Sydney Rock Oyster to the assessment of sediments. *Proceedings of the international Symposium on Environmental Chemistry and Toxicology* (*interSECT*), Sydney, NSW, 0108.

Levy, V., Smith, R., Stauber, J. and Binet, M. (2004) Manganese discharge from the Myuna Colliery. Hydrobiology Report CC/0401-Myuna-Mn, 100 pp.

Liu, P-C. and Chen, J-C. (1987) Effects of heavy metals on the hatching rates of brine shrimp *Artemia salina* cysts. *Journal of the World Aquaculture Society* 18, 78-83.

Macdonald, J.M., Shields, J.D. and Zimmer-Faust, R.K. (1988) Acute toxicities of eleven metals to early life-history stages of the yellow crab *Cancer anthonyi*. *Marine Biology* 98, 201-207.

Martin, J.L. (1976) Accumulation de Fe, Cu, Zn, Mg, Mn, et Co dans l'ovaire de *Carciuns maenus* L. au cours de l'ovogenese. *C.r. Séanc. Soc Biol Filiates* 170, 157-162.

Simon J and Laginestra E (1997). Bioassays for testing sublethal toxicity in effluents, using gametes of the sea urchin *Heliocidaris tuberculata.* National Pulp Mill Report Research Program Technical Report N^{o}20, Canberra, CSIRO, 36 pp.

Stauber JL, Tsai J, Vaughan GT, Peterson SM and Brockbank CI (1994). Algae as indicators of toxicity of the effluent from bleached euclaypt kraft pulps. National Pulp Mills Research Program Technical Report 3, CSIRO, Canberra.

Stauber, J.L., Jones, R.J., Binet, M.T. and King, C.K. (2002) The effect of nickel processing waste liquor on corals and their symbiotic dinoflagellates. CSIRO Energy Technology Investigation Report No. ET/IR474R, 34 pages.

Watling, H.R. (1983) Comparative study of the effects of metals on the settlement of *Crassostrea gigas*. *Bulletin of Environmental Contamination and Toxicology* 31, 244-351.

WHO (2004) Manganese and its compounds: environmental aspects. Concise International Chemical Assessment Document 63, International Program on Chemical Safety, World Health Organization, Geneva.

Young, L.G. and Nelson, L. (1974) The effects of heavy metal ions on the motility of sea urchin spermatozoa. *Biological Bulletin* 147, 236-246.