9 CONCLUSIONS

9.1 Summary

This report describes numerical modelling undertaken to determine the near and far field impacts of effluent discharge to Port Curtis from the proposed GPN processing plant at Gladstone. The focus has been water column quality responses to this discharge. As a result of an extensive investigation into a wide range of effluent disposal options, a proposed diffuser arrangement has been adopted that offers the best dilution and dispersal of pollutants considered to date.

This arrangement includes:

- In Stage 1: a single diffuser aligned perpendicular to the ambient tidal current direction, discharging the expected maximum flow for Stage 1 vertically upward the surface; and
- In Stage 2: two almost parallel diffusers aligned perpendicular to the ambient tidal current direction, each discharging half the expected maximum flow for Stage 2 (double Stage 1).

The results of both near- and far-field modelling tasks have been presented in previous sections. These have been presented in terms of relationships to WQOs, as timeseries and colour contour maps.

9.2 Modelling Assumptions and Limitations

In addition to those already discussed, modelling assumptions and limitations that need to be considered in interpretation of the results are as follows:

- In terms of manganese, we have applied a 10 day half life decay to its evolution. Application of no decay would increase reported concentrations.
- Natural variation in background concentrations could be significant in assessing the compliance or otherwise with WQOs, and a background monitoring programme should be considered.

We recommend that a detailed water quality monitoring programme be instituted prior to, and as part of, Phase 1 and Phase 2 works to assess the performance of the diffuser systems implemented. All the pollutants considered in this study should be included in such a program. BMT WBM is happy to provide input to the design and implementation of a monitoring program, and also to use results on an ongoing basis to refine and improve the modelling framework designed and executed as part of this study.

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APPENDIX A: MONITORING DATA IN PORT CURTIS

A summary of the 20th, 50th (median) and 80th percentiles of all *in-situ* measurements and laboratory analysis results from the water samples collected from each site in Port Curtis are shown in the table below. This data was collected between December 1998 and November 2001 at high water conditions, as part of the Marine Water Quality Programme (MWQP) in Port Curtis undertaken by WBM for Southern Pacific Petroleum (Development) Pty Ltd (SPP(D)).

Parameter	Unit	1 Boat Creek			2 Fishermans Landing			3 Gully C			4 Targinie Creek			5 Curtis Island (1)			6 Curtis Island (2)		
In-situ measurements: (20th percentile, 50th percentile, 80th percentile)																			
Temperature	°C	23.9	25.3	25.8	20.4	24.5	27.1	20.6	25.2	27.5	20.0	24.7	27.7	20.2	25.3	27.4	20.2	25.2	27.5
Conductivity	mS/cm	52.8	54.3	54.6	52.0	54.1	56.3	49.9	54.3	55.6	48.7	54.1	55.4	51.3	54.0	56.2	51.6	54.1	56.4
Salinity	g/L	34.7	36.0	36.2	34.3	35.9	37.3	32.8	36.0	36.9	31.9	35.9	36.8	33.8	35.8	37.1	34.0	35.8	37.4
pH	Units	8.0	8.1	8.1	8.0	8.1	8.2	8.0	8.1	8.2	7.8	7.9	8.0	8.0	8.1	8.1	8.0	8.1	8.2
Redox	mV	163.0	171.0	286.2	159.0	249.5	340.0	166.0	255.0	339.8	174.2	294.0	396.0	158.2	259.0	338.8	157.0	241.0	347.6
DO	mg/L	5.4	5.5	6.4	5.6	6.2	6.7	5.8	6.3	6.9	5.2	5.9	6.7	5.7	6.3	6.9	5.7	6.3	6.8
DO %	% Sat	81.0	82.7	92.7	85.9	89.3	96.3	86.9	90.5	98.8	80.3	85.7	93.2	87.0	91.0	100.1	87.0	90.5	99.0
Turbidity	NTU	6.9	14.7	15.2	10.9	19.3	32.9	6.2	9.4	27.2	9.3	13.5	30.8	12.5	24.3	36.7	11.2	22.9	35.8
Secchi Depth	m	1.1	1.2	1.3	0.9	1.0	1.3	0.9	1.1	1.3	0.9	1.0	1.2	0.6	0.8	1.0	0.8	1.0	1.1
Trace Elements:																			
Aluminium	µg/L	29	47	71	34	87	210	30	70	120	37	66	120	48	80	140	48	63	100
Arsenic	µg/L	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
Barium	µg/L	9	12	14	8	9	12	9	11	15	9	12	14	7	10	12	7	8	11
Boron	µg/L	4,200	4,500	5,000	4,200	4,540	5,100	4,100	4,600	5,000	4,100	4,500	5,100	4,100	4,500	5,000	4,200	4,500	5,100
Cadmium	µg/L	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
Chromium	µg/L	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
Copper	µg/L	<1	<1	<1	<1	<1	1.4	<1	<1	<1	<1	<1	1.2	<1	<1	1.4	<1	<1	<1
Iron	µg/L	22	46	100	24	76	320	27	51	180	35	87	170	43	110	270	20	67	140
Lead	µg/L	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
Manganese	µg/L	4	8	11	4	8	17	4	8	13	7	11	18	3	7	17	3	6	15
Mercury	µg/L	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Nickel	µg/L	<1	<1	1.3	<1	<1	2	<1	<1	1.4	<1	<1	2	<1	<1	3	<1	<1	2
Zinc	µg/L	<1	<1	3	<1	1.4	6	<1	<1	3	<1	<1	3	<1	1.1	3	<1	<1	4
Fluoride	µg/L	890	960	1,000	900	990	1,100	900	1,000	1,100	900	990	1,100	930	980	1,100	940	1,000	1,200
Compounds:																			
Cyanide	µg/L	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5
Nutrients:																			
Total Nitrogen	µg/L	130.0	180.0	280.0	140.0	180.0	240.0	140.0	210.0	251.2	140.0	200.0	278.0	140.0	200.0	290.0	130.0	180.0	270.0
Total Kjeldahl Nitrogen	µg/L	120.0	180.0	270.0	110.0	180.0	240.0	140.0	210.0	240.2	120.0	200.0	250.0	120.0	196.0	250.0	120.0	180.0	250.0
Organic Nitrogen	µg/L	90.0	150.0	210.0	100.0	160.0	220.0	115.2	172.5	221.6	110.0	170.0	230.0	110.0	180.0	230.0	120.0	150.0	240.0
Ammonia	µg/L	6.0	10.0	40.0	7.0	12.0	24.0	5.2	11.5	25.8	6.0	13.0	26.0	7.0	10.0	23.0	5.0	10.0	30.0
Nitrite	µg/L	<5.0	<5.0	5.0	<5.0	<5.0	9.0	<5.0	<5.0	5.0	<5.0	<5.0	5.0	<5.0	<5.0	5.0	<5.0	<5.0	5.0
Nitrate	µg/L	<5.0	<5.0	20.0	<5.0	7.0	13.0	<5.0	<5.0	5.8	<5.0	<5.0	5.0	<5.0	<5.0	20.0	<5.0	<5.0	18.0
Total Phosphorus	µg/L	10.0	12.0	14.8	10.0	12.0	19.0	10.0	11.5	18.8	10.0	12.0	15.6	10.8	16.0	22.6	10.0	11.0	15.2
Orthophosphorus	µg/L	<5.0	<5.0	7.0	<5.0	<5.0	8.0	<5.0	<5.0	9.8	<5.0	<5.0	9.0	<5.0	<5.0	8.0	<5.0	<5.0	9.0
Suspended Solids:																			
Suspended Solids	mg/L	9.0	17.0	34.0	14.0	36.0	56.0	12.0	17.0	43.0	14.0	31.0	51.0	18.0	36.0	62.0	17.0	25.0	59.0

These data have also been combined with more recently collected information by URS. Revised conditions are presented in the following table. Where species are not listed, no additional data was available and the statistics above hold.

Parameter	Minimum	20th %ile	Median	80th %ile	Maximum	n
Turbidity (NTU)	1.0	5.0	12.0	27.0	225.0	946
Chlorophyll-*a* (µg/L)	0.33	1.07	1.87	4.85	11.36	127
Dissolved Oxygen (%sat)	71.5	91.5	94.5	99.7	128.1	1035
pH	4.73	7.88	7.99	8.13	8.60	1032
Suspended Solids (mg/L)	2.0	12.0	24.0	48.0	116.0	331
Conductivity (mS/cm)	23.6	52.4	54.9	56.6	60.5	1036
Temperature (°C)	17.0	22.4	25.9	29.2	35.5	331
Ammonia (µg/L)	2.5	7.0	11.0	30.4	200.0	189
Nitrates and Nitrites (µg/L)	5.0	5.0	5.0	25.0	422.5	195
Total Nitrogen (µg/L)	25.0	140.0	190.0	270.0	2300.0	194
Filterable Reactive Phosphorous (µg/L)	2.5	2.5	2.5	10.0	50.0	192
Total Phosphorous (µg/L)	5.0	10.0	25.0	25.0	32.0	194
Aluminium (µg/L)	2.5	35.0	73.0	140.0	3,700.0	
Iron (µg/L)	2.5	31.6	90.0	210.0	2,100.0	174
Nickel (µg/L)	0.5	0.5	0.5	1.5	20.0	174
Manganese (µg/L)	0.5	3.9	7.6	15.0	59.0	194
Zinc (µg/L)	0.5	0.5	0.5	3.3	14.0	174

APPENDIX B: KEY LIMITATIONS AND RECOMMENDATIONS

MEMORANDUM

TO: Chris Pigott – URS Australia Pty Ltd

FROM: Fanny Houdré / Dr Michael Barry

DATE: 17 October, 2007

SUBJECT: **GPN Modelling – Recommendations for further work/modelling**

This memorandum refers to the final report by WBM on the Gladstone Pacific Nickel Modelling in October 2007 (R.B16019.004.05.doc). Those items not applicable to the current report have been greyed and italicised.

Each model used in that study has limitations that need to be considered in interpretation of the results, and further modelling in both the near and far field will be necessary at a later stage to better inform the detailed design process. Key limitations and recommendations for further work/modelling are described below.

Hydrodynamics

Hydrodynamic impacts of the discharge (from a far-field perspective) were captured within the modelling framework by including the volumetric inputs in the hydrodynamic simulations. Importantly, these simulations were run for a 2 week period, and then results were cycled over the multi-month advection-dispersion modelling period. As such, the entire modelling period was not explicitly simulated in the hydrodynamics. The primary reason for this was the long model run times, which were in the order of 4 days elapsed time to execute two weeks simulation time. At this speed, approximately 80 days would be required to run the hydrodynamic model over multi-month, which was not feasible within the study timeframes.

Dispersion Coefficients

Spatially variant dispersion coefficients employed in the far field model were adopted based on dye tracer studies previously undertaken by WBM. Whilst representing the best possible dispersion schematisation available for the area, further dye tracer studies should be considered to improve confidence in the model results. In particular, now that the location of the diffusers is better defined, attention should be given to refining dispersion coefficient estimates in the immediate vicinity, upstream and downstream of the discharge zone. This could be undertaken with dye tracer studies, or drogue track experiments.

Boundary Return Coefficients

The modelling has shown that the effluent discharged from the proposed GPN outfall interacts with a large portion of Port Curtis. The effluent is also predicted to exit the model domain at the ocean boundary. As such, the far field modelling framework has required specification of a 'return coefficient’ for effluent crossing the boundary. This coefficient describes the proportion of effluent returning to model, as a function of the exiting concentrations. For this study we have assumed a coefficient of 0.3, consistent with other WBM studies, however we recommend that the sensitivity of the model results to this coefficient be investigated.

Two Dimensional Modelling

The far field model used adopted a depth averaged schematisation. This means that the model cannot resolve vertical distributions of velocity or constituents, but rather, computes a depth averaged approximation. This is satisfactory in terms of ambient flow descriptions, but may not exactly hold in the immediate vicinity of the outfall if the effluent is not well mixed.

For example, the far field model is schematised so that it receives the effluent as an element load at the specified locations, and this element load is, by definition, immediately mixed over the entire model depth. During times of high ambient velocity it is expected that the diffuser arrangement will ensure full vertical mixing relatively near to the outfall, making this depth averaged approximation acceptable. This approximation may be less applicable at times of slack tide and low tidal velocities.

Element Inflows

In addition to the above, the far field model also mixes the effluent discharge over the entire breadth and width of each receiving element. This leads to some immediate dilution (in addition to the depth averaging) of the effluent across the elements of concern. The best way to reduce the impact of this effect is to reduce the lateral dimensions of the elements receiving effluent loads (i.e. refine the computation mesh detail), to minimise the artificial initial lateral mixing. Doing so, however, leads to increased simulation times and more cumbersome results interrogations. Results should be interpreted accordingly.

Given the quasi-exploratory nature of this study, and the already very large computational requirements of the model mesh, it was not feasible to undertake this element refinement at each newly investigated outfall location. As such, this refinement has not been undertaken here for the currently preferred outfall location, and results should be interpreted accordingly. On selection of a final outfall location, however, this refinement should be considered to ensure consistency of results.

Additive Effects

Discharge concentrations for the near and far field modelling have been supplied by GPN. These have been applied in both models and added, to capture the potential fro recirculation and accumulation in the model domain. This represents a rigorous approach to the assessment of impacts as it captures long term increases in ambient (background) pollutant concentrations and the influence that these have on the efficiency of near field mixing processes.

No investigation of the potential for recirculation has been undertaken as part of this study, but should be considered in future works. One way to examine this potential recirculation behaviour is through computational fluid dynamics (CFD) analyses. WBM can provide assistance in this regard if required.

Steady State Analysis

The near field modelling is essentially a steady state analysis that cannot take account of the influence of the dynamic ambient tidal conditions on plume evolution. To some extent this has been captured in the far field model, but only within the previously described depth and lateral averaging assumptions. It is recommended that the dynamic evolution of the near field plume be further investigated as part of subsequent design works. Again, CFD analysis may assist in this regard.

Near Field Interrogation Point

It was agreed with GPN to interrogate the near field results at several points from the diffuser. Resultant pollutant concentrations have been computed at these points and compared to WQOs. It should be noted that resultant concentrations will clearly be higher than reported at locations closer to the diffuser, and this may warrant further investigation at a later stage.

Diffuser Plume Interaction

The current proposal for effluent discharge involves use of several diffuser lines. The interaction of these plumes cannot be investigated using the near field model, and as such the far field model is the only current means of investigation of potential overlap and interaction processes. The far field model, however, has depth and lateral averaging limitations in this regard. Whilst the far field model captures total mass loads correctly, it was not intended for use as a tool to investigate the details of plume interaction in the near field.

A detailed analysis of the implications of potential overlap and interaction processes of plumes has not been possible as part of this study, particularly in a dynamic environment. Reported concentrations and dilutions in the near field have not taken account of potential overlap. This issue should be considered in the future, using the CFD model or some other agreed investigative tool.

Regards,

Fanny Houdré/Michael Barry

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Marine Environment Reports

Appendix B

	Author	Report Name	Date
B1	M. Adams, S. Apte, A. Steinberg, L. Andersen, C. Jarolimek	Manganese Oxidation in Port Curtis, Central Queensland	September 2007
B2	S. Apte	Manganese (II) Oxidation Rates in Seawater – a Review	November 2006
B3	S. Apte	Manganese Reactions in Seawater – Additional Information	December 2006
B4	S. Apte, M Adams, F. Melville, L. Andersen, L. Hales	Manganese Oxidation Study	March 2007
B5	J. Stauber and M. Binet	Bioaccumulation of Manganese and Toxicity of Manganese Dioxide in Marine Waters	December 2006
B6	J. Stauber	Derivation of a Manganese Trigger Value for Port Curtis, Queensland	October 2006

Marine Environment Reports

Appendix B1- Manganese Oxidation in Port Curtis, Central Queensland

Manganese Oxidation in Port Curtis, Central Queensland

Merrin S. Adams, Simon C. Apte, Anja Steinberg[1], Leonie Andersen[1], and Chad Jarolimek

CSIRO Land and Water Science Report 07/65
September 2007

Gladstone Pacific Nickel Limited

Commercial-in-confidence

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EXECUTIVE SUMMARY

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

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

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

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

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

The findings of the study were as follows:

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

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

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

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

TABLE OF CONTENTS

1 INTRODUCTION

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

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

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

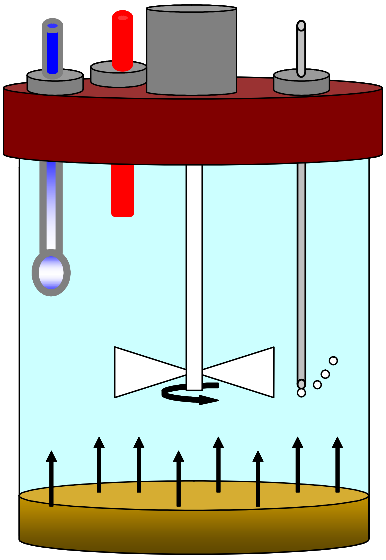

Figure 1. Schematic diagram of a benthic core stirrer-reactor.

2 EXPERIMENTAL

2.1 General Notes

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

2.1.1 Sample Collection

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

2.1.2 Oxidation of Manganese in Seawater

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

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

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

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

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

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

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

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

2.1.3 Biological Oxidation of Manganese in Tidal Mangrove-lines Mudflats

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

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

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

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

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

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

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

[a] No added manganese

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

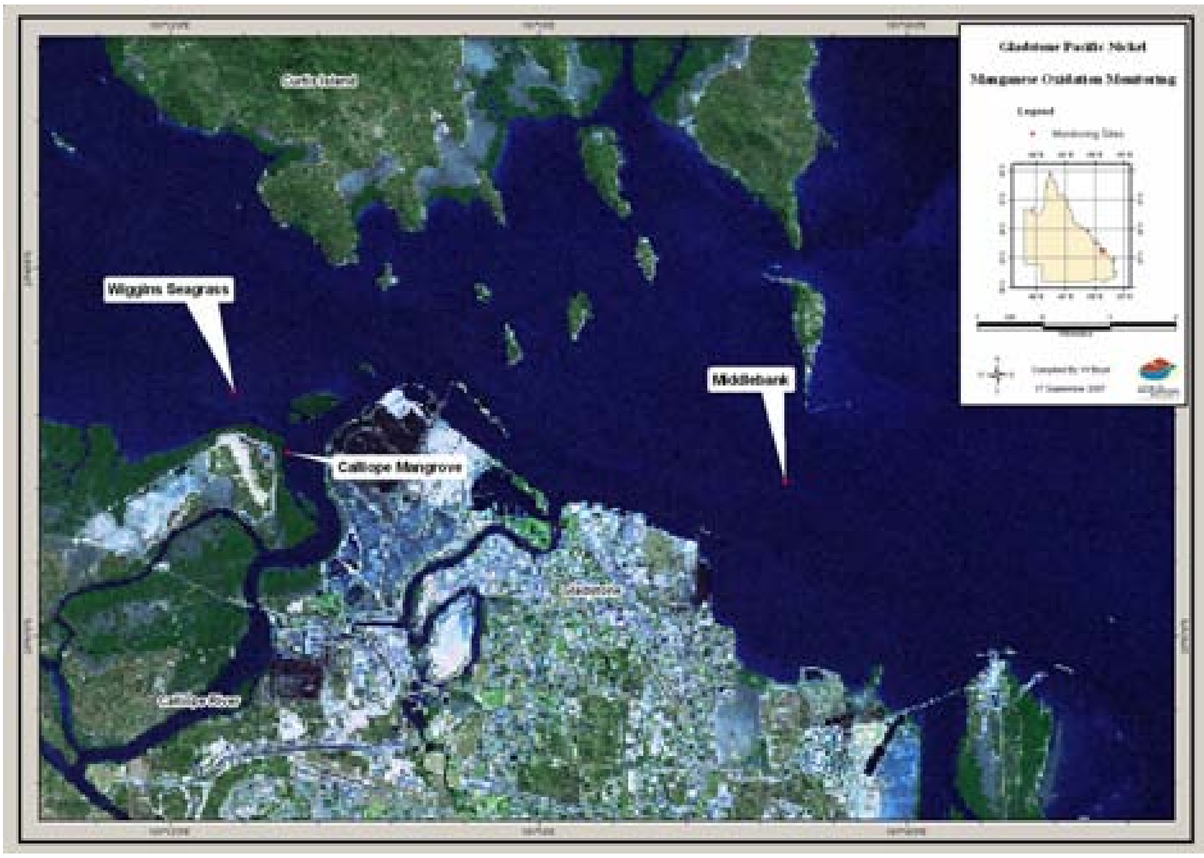

Figure 2. Locations of the benthic corer-reactor sampling sites.

2.1.4 Biological Oxidation of Manganese in Different Sediment Types

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

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

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

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

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

[a] No added manganese

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

2.1.5 Analysis of Manganese and Total Suspended Solids

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

3 RESULTS AND DISCUSSION

3.1 Oxidation of Manganese in Seawater

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

Table 1. Suspended sediment concentrations of the incubation treatments

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

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

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

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

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

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

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

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

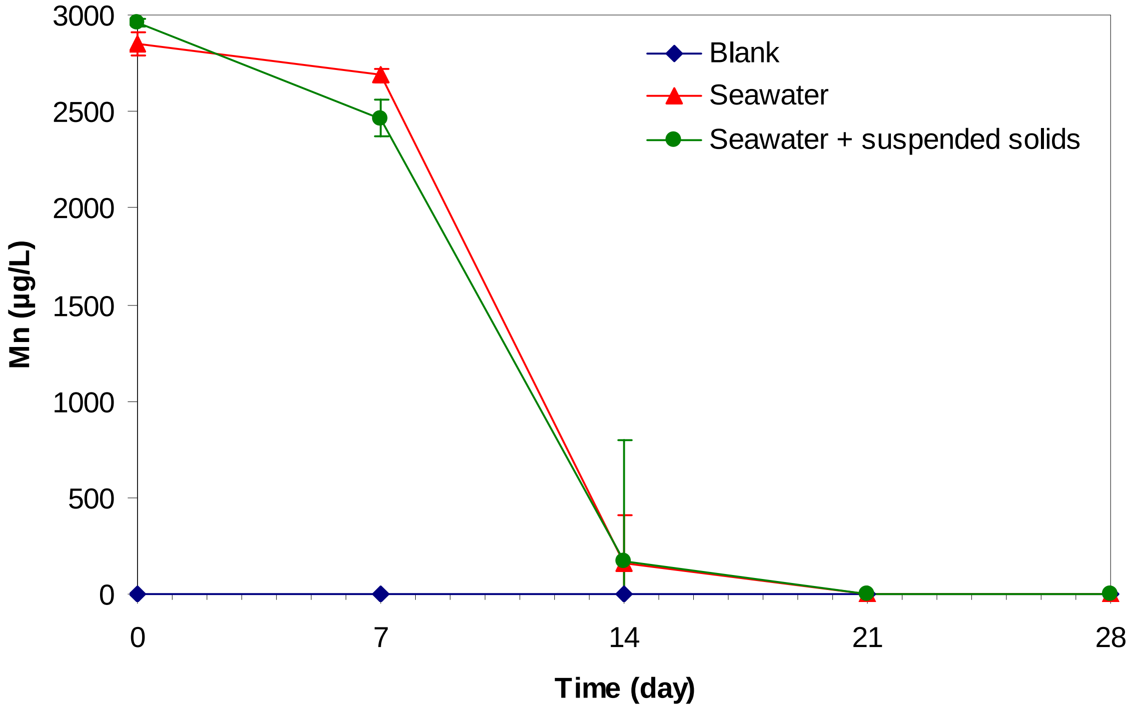

Figure 3. Variation of dissolved Mn concentrations with time during the long-term incubation experiments in seawater ± suspended solids (67±3 mg/L). Data points represent the mean of triplicate treatments. Data point for blank represents data from one replicate. Error bars show one standard deviation.

3.2 Benthic Sediment Studies

3.2.1 Tidal mangrove-lined mudflats

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

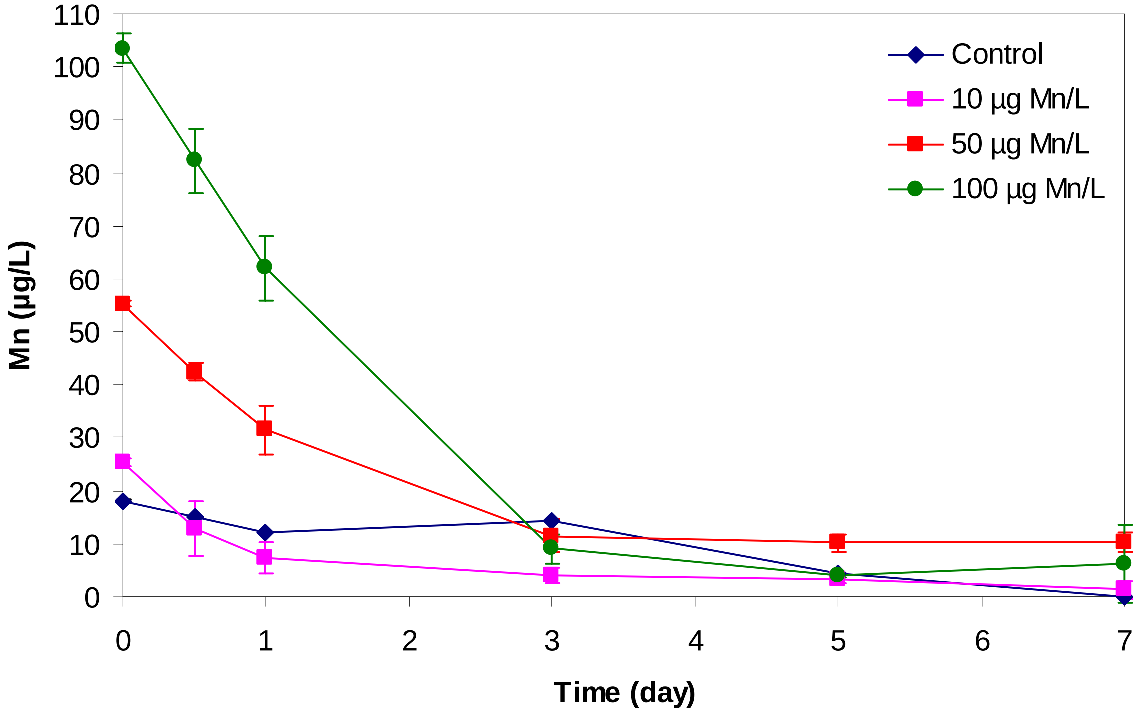

Figure 4. Change in dissolved Mn concentrations with time during the benthic corer-reactor experiments with sediments from tidal mudflats. Data points represent the mean of duplicate samples from two cores (n=4). Data point for Control represents the mean of duplicate samples from one core. Error bars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

3.2.2 Middlebank and Wiggins Island sediment samples

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

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

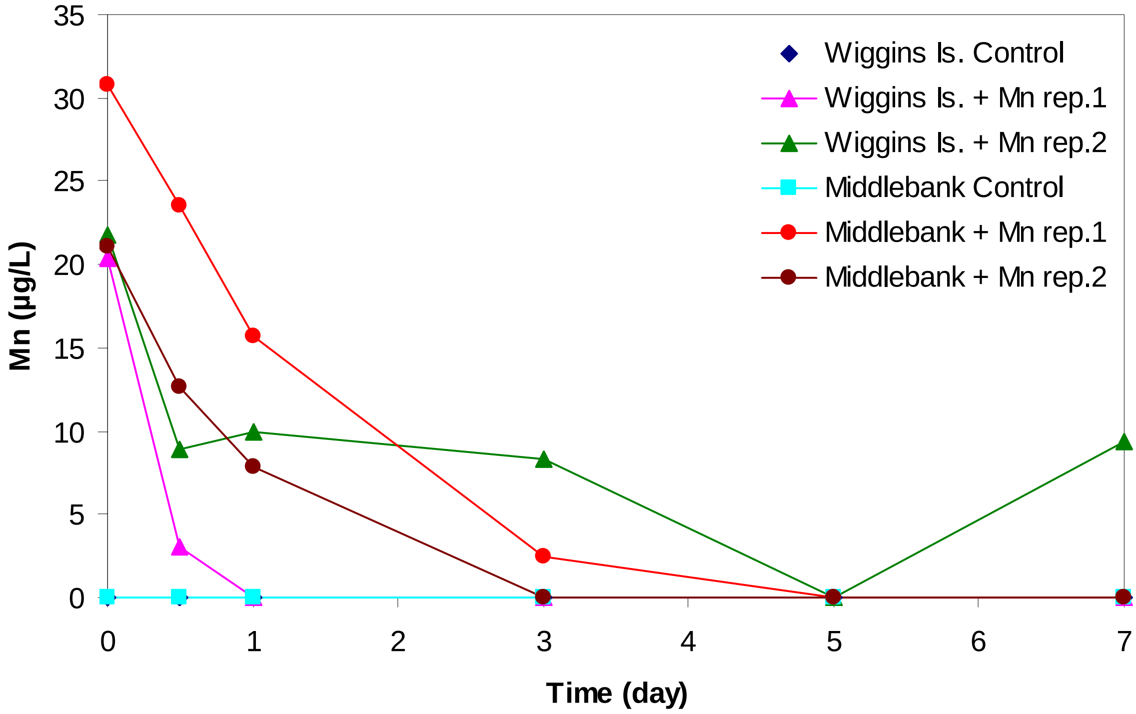

Figure 5. Variation of dissolved Mn concentration with time during the core-reactor experiments with sediment from Wiggins Island (seagrass bed, silt/clay sediment with fine sand) and Middlebank (coarse sand). Data from each individual core is shown. Each data point represents the mean of duplicate samples.

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

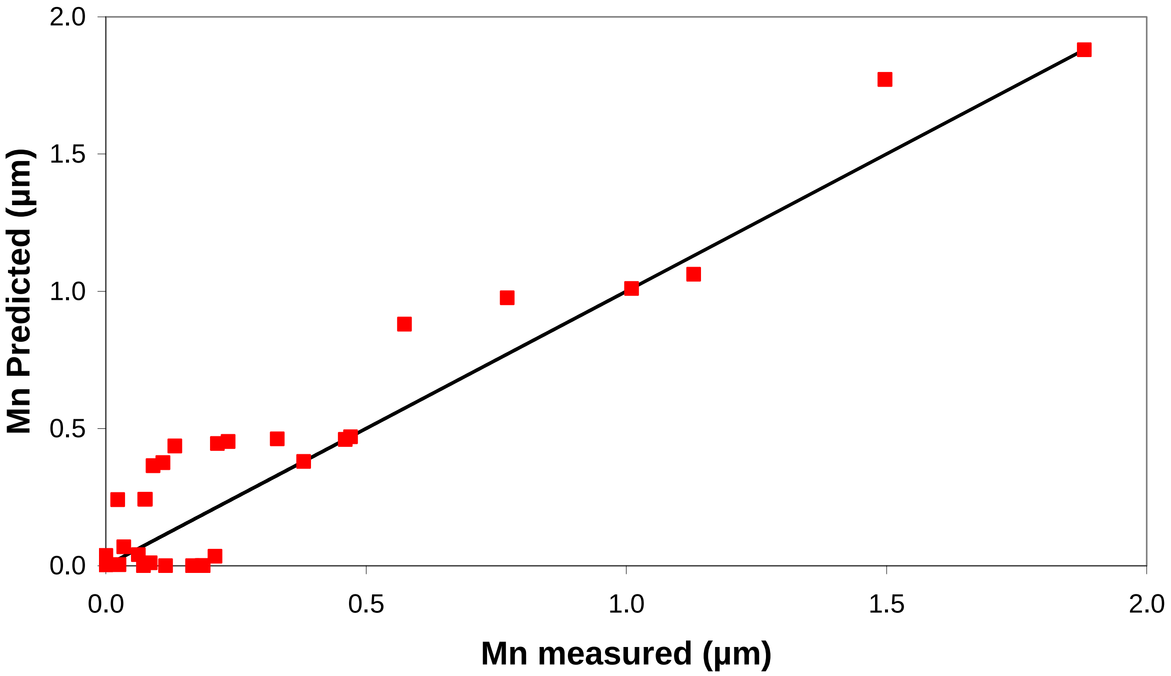

Figure 6. Benthic corer-reactor data plotted against dissolved manganese concentrations predicted using the Morgan heterogenous rate equation ($y = 1.0254x + 0.0495$, $R2 = 0.9009$). The solid line is the line of equivalence. If model predictions were perfect, all data would fit on this line.

4 CONCLUSIONS

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

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

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

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

5 ACKNOWLEDGEMENTS

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

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7 APPENDIX 1 - EXPERIMENTAL DATA

A. Adsorption study data

10 µg/L Mn Added

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

100 µg/L Mn Added

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

B. Long-term oxidation rate in seawater

(All Mn concentrations are in µg/L)

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

C. pH and Dissolved Oxygen Concentrations

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

D. Benthic Corer Reactor Experiments

(All Mn concentrations are in µg/L)

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

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

E. Wiggins Island Seagrass Beds and Middlebank Sites

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

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

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

Corer-reactor experiments: Oxygen, pH and TSS data

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

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

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

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Marine Environment Reports

Appendix B

Appendix B2- Manganese (II) Oxidation Rates in Seawater – a Review

Manganese(II) Oxidation Rates in Seawater – a Review

Final Report, 12 November 2006

Simon C Apte
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Lucas Heights, Menai NSW 2234

Background

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

Recent predictions of plant operation indicate that the plant may discharge process waters into Port Curtis which could contain 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 literature search was conducted and the relevant references critically reviewed. Based on this information, dissolved manganese oxidation rates relevant to the Port Curtis system are discussed.

Forms of manganese in seawater

Manganese speciation in natural waters is generally dominated by the Mn(II) and Mn(IV) oxidation states. The interconversions between these forms is of particular importance to the aquatic chemistry of manganese as Mn(II) species are soluble whereas Mn(IV) readily forms insoluble oxides.

The main oxidant in natural waters is dissolved oxygen:

$$4\ \mathrm{Mn}^{2+}\ (aq) + \mathrm{O}_2\ (aq) + 6\ \mathrm{H}_2\mathrm{O} = 4\ \mathrm{MnOOH}(s) + 8\mathrm{H}^+$$

The rate of oxidation is depends on the solution oxygen concentration and is strongly pH dependent (oxidation increases with increasing basicity). Rates of abiotic oxidation in aqueous solution are very slow. Oxidation is quicker in the presence of various particulate surfaces which may catalyse the reaction (Morgan 2005, Yeats and Strain 1990).

The oxidation of Mn(II) can occur by direct chemical oxidation (abiotic pathway) and by bacterially-catalysed routes. Mn(II) is oxidised by a wide variety of bacteria and the rates of oxidation are much higher than by abiotic pathways. Microbially-catalysed oxidation rates are up to five orders of magnitude greater than abiotic rates (Tebo et al. 2005). Sunlight may play a role in inhibiting the rate of bacterially mediated Mn(II) oxidation (Sunda and Huntsman 1990). Rates of Mn(II) oxidation are higher in the dark when compared to light which can lead to pronounced diurnal cycle in oxidation rates (Sunda and Huntsman 1990).

Kinetic expressions for Mn(II) oxidation

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

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

The concentration of Mn^{2+} at time t may be calculated by integrating (1):

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

Where:

k = conditional rate constant

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

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

t= time

The conditional rate constant is dependent on the oxygen concentration and the square of the hydroxyl concentration, in other words, oxidation becomes progressively faster in solutions of increasing basicity. This equation was used by von Langen et al. (1997) to successfully model Mn oxidation in open ocean waters.

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

$$-d[Mn^{2+}]/dt = k_1[Mn^{2+}][O_2] + k_2[Mn^{2+}][Mn_p][O_2] \qquad (3)$$

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°C increase in temperature (Yeats and Strain 1990). The above equation includes terms for both homogenous oxidation and heterogeneous autocatalytic mechanism. 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.

Field measurement of oxidation rates in seawater

On the basis of field measurements, Yeats and Strain (1990) were able to deduce rate constants using equation (3) for the reaction of Mn(II) with oxygen in cold marine waters. The rate equations and rate constants they calculated for the reactions at an ambient temperature of 1.5°C and a pH of 8.0 were:

$k_1 = = 9.78 \pm 4.86 \times 10^{-5}\ \mu M^{-1}\ d^{-1}$,

$k_2 = 3.19 \pm 0.65 \times 10^{-3}\ \mu M^{-2}\ d^{-1}$.

The above constants were adjusted by Overnell et al. (2002) by assuming that a 11°C increase in temperature results in a 2-fold increase in rate constant and were used to calculate Mn oxidation rates in a Scottish Loch. Removal times for dissolved Mn of 7-25 days were calculated. The highest oxidation rate was ca. 0.07 Md^{-1}.

Calculation of Mn(II) oxidation rates in Port Curtis

The literature search indicated that there were no directly relevant scientific reports or papers relating to the oxidation of ppm concentration Mn discharges in seawater. In order to identify the rates of oxidation relevant to Port Curtis a range of kinetics calculations were therefore performed using equations (1) and (3). The integrated form of equation (3) was used (Sung and Morgan 1980) which is derived based on the assumption that Mnp = [Mn]*i* – Mn(II)]. The constants derived by Yeats and Strain (1990) were adjusted to a water temperature of 24°C. The spreadsheet calculator was checked using the data for Loch Etive, Scotland supplied by Overnell et al. (2002) leading to quite reasonable calculations.

The first calculation was performed assuming that the homogenous oxidation reaction prevails. The following conditions were used:
$k = 4 \times 10^{12}$ M^{-3} d^{-1} (as recommended by Morgan 2005).
Initial Mn concentration was 20 µM (1100 µg/L)
Dissolved oxygen 213 µM, pH 8.2, temperature 25°C

Results indicated that the half-life of Mn(II) was typically 350 days. This value is consistent with the data summarised by Morgan (2005) who noted that the homogenous oxidation of manganese in seawater is slow.

The second calculation assumed that the autocatalytic reaction and bacterial catalysis prevails:
k_1 = 2.93E-04 μm^{-1} d^{-1}
k_2 = 9.57E-03 μm^{-2} d^{-1}
Initial Mn concentration was 20 µM (1100 µg/L)
Dissolved oxygen 213 µM, pH 8.2, temperature 24°C

Results indicate that the half life for Mn(II) was about 3 hours. The oxidation rate is higher than other reported rates (Yeats and Strain 1990, Overnell et al. 2002) because of the higher water temperature and the much higher initial manganese concentration. In the author's opinion, this calculation is likely to overestimate Mn(II) oxidation. This is because bacterial oxidation may be saturated at relatively low Mn(II) concentrations. Also calculations are sensitive to the initial Mn concentration which is particularly high in the modelled scenario. It should also be noted that there is a question mark over the appropriateness of k_1 and k_2 constants. These constants were derived for low manganese concentrations in cold marine waters and may not be relevant to Port Curtis. No other suitable rate constants were found in the literature.

Conclusions

1. There is a paucity of relevant information in the published literature. The kinetic expressions developed by Morgan (2005) are suitable for modelling purposes but the choice of reaction pathway and selection of constants is critical.

2. Based on a critical review of the literature and CSIRO experience in this area, the oxidation of Mn(II) in seawater should be relatively slow and generally occurs over timescales of weeks/months. The slow oxidation rate in seawater is supported by the absence of any reports of visible manganese precipitation in coastal waters.

3. In the absence of measured rate constants which are relevant to the system, it is recommended that a half-life of 28 days for Mn(II) in the waters of Port Curtis is used for

fate/transport modelling processes. This is a crude estimate based on best professional judgement.

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Appendix B3- Manganese Reactions in Seawater – Additional Information

Manganese Reactions in Seawater – Additional Information

8 December 2006

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1. Background

Gladstone Pacific Nickel Limited (GPNL) are undertaking technical feasibility and environmental impact studies as part of 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 mg/L 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 literature search was conducted and the relevant references critically reviewed (Apte 2006). Based on this information, dissolved manganese oxidation rates relevant to the Port Curtis system were recommended. The review also identified a number of uncertainties. Additional information was subsequently requested by the client on the following issues:

(i) The propensity for manganese dioxide particles to aggregate into larger particles that may precipitate in Port Curtis
(ii) The effect of Mn(II) oxidation on dissolved oxygen levels in the water column
(iii) The affinity of other metals for manganese oxide and their stability in marine sediments or during digestion.

This technical note addresses these questions.

2. Manganese dioxide precipitation and particle aggregation

An extensive literature search indicated little information on the precipitation of manganese-rich discharges in marine systems. However, Neretin et al. (2003) studied manganese dynamics in the Baltic Sea and characterised manganese particle formation. The underyling anoxic waters contained high concentrations of dissolved manganese (typically 0.8-1.0 mg/L). Significant precipitation occcured when the dissolved manganese diffused to the upper, oxygenated layers of the water column. Two different types of manganese-rich particle were identified by microscopy – amorphous particles (92% of total) and particles with dendritic (stellate) structures (8% of total). About 68 % of all Mn particles were associated with large aggregates which also contained organic matter. Each aggregate contained between 3-16 particles with a median of 6. The remaining 32% of particles were in free suspension.

The mean equivalent spherical radius of Mn-rich aggregates was 16.6±9.0 µm. Amorphous particles had a mean spherical radius of 1.8±0.5 µm and the stellate particles averaged 4.2. ±1.2 µm. Neretin et al. (2003) used a weighted mean particle size of 4 µm in Stokes Law settling rate calculations. The derived settling rate was 0.98 m/day is probably an upper limit estimate as the precipitates are not solid spheres and the density of crystalline manganese dioxide (birnessite, 3.0 g/cm^{-3}) was used in the calculation.

3. Effect of Mn(II) oxidation on dissolved oxygen levels in the water column

Manganese speciation in natural waters is generally dominated by the Mn(II) and Mn(IV) oxidation states. The interconversions between these forms is of particular importance to the aquatic chemistry of manganese as Mn(II) species are soluble whereas Mn(IV) readily forms insoluble oxides. The main oxidant in natural waters responsible for the oxidation of Mn(II) to Mn(IV) is dissolved oxygen:

$$4\ \mathrm{Mn}^{2+}\ (aq) + \mathrm{O}_2\ (aq) + 6\ \mathrm{H}_2\mathrm{O} = 4\ \mathrm{MnOOH}(s) + 8\mathrm{H}^+$$

As can be seen, 1 mole of O_2 oxidises 4 moles of Mn(II).

Note that: 1 mmole of oxygen = 32 mg/L
1 mmole of Mn(II) = 56 mg/L

If manganese(II) oxidation was rapid, a discharge containing 10 mg/L Mn(II) would therefore consume 1.4 mg/L of dissolved oxygen. The concentrations of oxygen in natural coastal seawaters are typically 6-7 mg/L so this represents at worst a 22 % depletion of dissolved oxygen concentration. If one makes the reasonable assumption that Mn(II) oxidation kinetics will be slow relative to the mixing time for atmospheric oxygen to equilibrate with seawater and there is good circulation of seawater, Mn(II) discharges in the 1-10 mg/L concentrations range are unlikely to significantly deplete dissolved oxygen concentrations in the water column.

4. Affinity of metals for manganese oxides and stability of these complexes

The adsorptive affinity of manganese oxides for trace metals has been studied widely. Manganese oxide precipitates possess large surface areas and are effective adsorbents for many trace metals. Manganese dioxide has a point of zero charge (pzc) of typically 1.5, and at seawater pH is negatively charged (Balistrieri and Murray 1982). Anions such as chloride and sulphate do no adsorb to manganese dioxide as their specific adsorption energy is insufficient to overcome the electrostatic repulsion of the negatively-charged surface. In seawater at pH 8.0, 84.4% of the surface manganese oxide sites are bound by protons, 8.4% by Mg, 4.6% by Ca, 1.6% by Na and 0.6% by K (Balistrieri and Murray 1982). The sorption affinity sequence of trace metals for amorphous manganese oxides is typically:
$\mathrm{Cd}^{2+}<\mathrm{Ni}^{2+}<\mathrm{Zn}^{2+}<\mathrm{Cu}^{2+}<\mathrm{Co}^{2+}<\mathrm{Mn}^{2+}<\mathrm{Pb}^{2+}$ (Tonkin et al. 2004)
This sequence is similar to that reported for iron hydroxides with the exceptions of Mn^{2+} and Co^{2+} which adsorb more strongly to manganese oxides. Partition coefficient values for the adsorption of various trace metals onto synthetic manganese dioxide in seawater are shown in Table 1. These values may be used for the modelling of metal adsorption reactions. Alternatively, a more sophisticated surface complexation modelling approach has recently been developed by Tonkin et al. (2004).

Table 1. Log Kd values for trace metal adsorption onto synthetic manganese oxide (buserite), pH 7.3 ±0.3, equilibration time 45-50 days (Balistrieri and Murray 1986).

Metal	Log Kd
Pb	7.4
Zn	6.1
Co	6.0
Mn	5.8
Cd	4.7
Ni	4.3

In anoxic sediments and waters reduction of manganese oxides readily occurs leading to the dissolution of Mn oxides and the release of associated metals. This phenomenon is well known in aquatic systems (Neretin et al. 2003). In marine systems, HS^-, can act as a very effective reductant as the reduction kinetics are very fast, with half-lives in the order of seconds to minutes. Dissolved iron(II) if present at sufficient concentration may also act as a reductant (Neretin et al. 2003).

Substantial release of metals will also occur on the acidification of manganese-rich particles to values below the pH adsorption edge. As can be seen from Figure 1, the adsorption edge for trace metals varies from ca. pH 2 for lead to pH 7 for cadmium. These pH values are unlikely to occur in most coastal water environments. The information in Figure 1 also indicates that acidification of precipitates during laboratory analysis to pH values <2 will lead to the release of adsorbed metals.

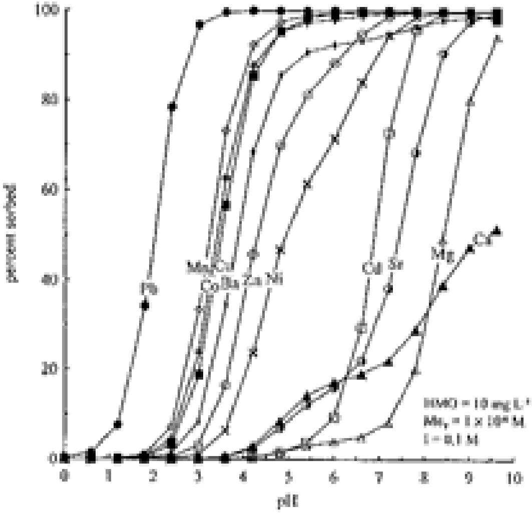

Figure 1. Predicted sorption edges from trace elements on manganese oxides in aquous solutions (Tonkin et al. 2004).

5. Conclusions

1. Based on a study conducted in the Baltic Sea (Neretin et al. 2003). The oxidation of Mn(II) in seawater will produce small particles of typically <4 µm diameter. Some of these particles will aggregate (especially in the presence of organic matter) and form composite particles

with a diameter of typically 20 µm. In tidal coastal environments, it is unlikely that these particles will settle from the water column.

2. Simple mass chemical calculations indicate Dissolved Mn concentrations in the 1-10 mg/L range are unlikely to cause any significant depletion of dissolved oxygen in coastal seawaters. Tidal mixing and the slow oxidation kinetics of Mn(II) will also reduce the impact on dissolved oxygen concentrations.

3. Most trace metals have a strong adsorptive affinity for manganese oxides. Partition coefficients have been derived which allow the prediction of metal adsorption in seawater. In reducing environments containing reductants such as sulphide and iron(II), particulate manganese readily dissolves, releasing adsorbed metals into solution. Acidification of particles also releases adsorbed metals into solution.

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Appendix B4- Manganese Oxidation Study