Memorandum

To:	Sophie Gray, T & T Landfills, Ltd	Date:	15 August 2019
From:	Dr Jason Park	Our Ref:	SCJ202PRO/T_T Water JP
Subject	Iron and manganese management options at the T&T landfill leachate treatment wetland		

The brief for the investigation was to:

- Assess water quality monitoring data (mainly Fe and Mn) at the landfill leachate treatment wetland, and
- Explore some practical options to improve iron (Fe) and manganese (Mn) management at the T & T Landfill wetland site.

Relevant background information provided by Sophie Gray (and Ray O'Callaghan) includes;

1. Wetland water quality testing results (10th May 2019 and 1st August 2019, Appendix 1),
2. In-situ physico-chemical measurements including Dissolved Oxygen (D.O), pH, Temperature and conductivity at eight locations around the constructed wetland (1st August 2019, Appendix 2),
3. Photographs of the constructed wetland (Figure 1) and an aerial photo showing potential downstream wetlands (Appendix 3),
4. Long-term dissolved Fe and Mn monitoring data (between June 2012 and July 2019) at the site 'TTD' located about 80 m below the wetland outlet (Figure 2),
5. Quarterly environmental monitoring report (Fountain 2019), and
6. Approximate water volume: 590 m^3; surface area: 620 m^2; water depths: 0.95-2.75 m; measured wetland outflow rate: 13.5 litres/s (or 1166.4 m^3/d); detention time of the wetland: 12.2 h.

In the quarterly environmental monitoring report, Fountain (2019) reported that while contaminant levels in the tributary below the landfill are mostly within an acceptable range, the sum of dissolved Fe and Mn has consistently exceeded the guideline value of 1 g/m^3. Fountain (2019) also pointed out that water from the two upstream dams at 'TTW' and 'TTE' continues to seep under the landfill, which is likely contributing to the elevated level of dissolved Mn in the downstream TTD. In particular, during heavy rainfall a proportion of flow continues to move through the landfill resulting in elevated concentrations of dissolved Mn.

Figure 1: Photographs of the constructed wetland treating T & T landfill leachate.

Assessment of Fe and Mn removal in the constructed wetland

Water pH, total/dissolved Fe and Mn concentrations in the inflow and outflow of the constructed wetland on the 10th May and 1st August 2019 are summarized in Table 1 (the entire range of water quality testing results are attached in Appendices 1 and 2).

There were minimal changes in Fe and Mn concentrations through the wetland on the 10th May 2019, with total Fe in the wetland influent and effluent of 6.3 and 6.7 g/m^3 and Mn concentrations of 2.4 and 2.5 g/m^3 respectively. The only change was the increase in dissolved Fe from 0.05 g/m^3 in the inflow to 3.1 g/m^3 in the outflow. This may indicate anaerobic/anoxic conditions at the base of the wetland (this is a supposition, as no DO data was available on the 10th May), which may have resulted in dissolution of Fe (II) at the wetland sediment, thereby increasing the dissolved Fe concentration on the wetland effluent (Davison et al. 1982; Prairie et al. 2001). In contrast, on the 1st August 2019 dissolved Fe concentrations in the wetland were reduced from 0.8 to 0.29 g/m^3 when the DO level around the wetland (Site 1-7, Appendix 2) was maintained at ~10% saturation. However, total Fe removal was still minimal (Total Fe_{in}: 4.4 g/m^3; Total Fe_{out}: 3.7 g/m^3, Table 1).

The minimal Fe and Mn removal in the constructed wetland is likely due to transient periods of anoxia when oxidative processes that promote removal are not operating. Aerobic conditions promote the formation of insoluble iron hydroxide and manganese (IV) especially at high pH, which is the dominant abiotic Fe and Mn removal process in constructed wetlands (Wiseman and Edwards 2004; Lesley et al. 2008).

As can be seen in Figure 1, the wetland has very sparse emergent vegetation cover, which is likely due to deepening the wetland to increase the detention time (Sophie Grey 2019, pers comm.). This suggest that the reduced wetland plants and substrate may have decreased adsorption surfaces for the Fe and Mn removal (i.e., predominantly filtration or precipitation) and potentially also limited oxygen release from roots for Fe and Mn oxidation.

During the monitoring period between August 2018 and May 2019 the sum of dissolved Fe and Mn concentrations at 'site TTD' (located about 80 m below the wetland outlet) has consistently exceeded the recommended guideline of 1 g/m^3 (Figure 2). Dissolved Mn concentrations have remained high at between ~1.5 and 4.2 g/m^3, but dissolved Fe concentrations were greatly reduced from 3.1 g/m^3 at the wetland outlet to below 0.1 g/m^3 at 'site TTD' 80 m downstream. This result suggests that oxygenation in the stream receiving the wetland effluent is sufficient (indicated by 56.4% DO saturation at Site 8, O'Brien (2019)) for biotic/abiotic Fe oxidation leading to formation of insoluble iron hydroxide flocs, which precipitate on the stream bed (a brown or brown/orange precipitate observed in the upstream of the site TTD, Fountain (2019)).

The passive removal of manganese is generally considered to be a much more difficult task than removal of iron (Hedin et al. 1994b; Lesley et al. 2008). Hedin et al. (1994b) reported that Mn removal is between 20 and 40 times slower than that for Fe in a range of treatment systems, which is largely due to the conditions required for the oxidation of manganese. The abiotic oxidation of manganese requires pH above 8, and even then is very slow at pH ~9.0 (Stumm and Morgan 1996), which is clearly not achievable within the wetland treatment systems. However, microbial processes occurring in natural biofilms and at the sediment surface can enhance Mn removal under more circum-neutral pH conditions (Pinsino et al.), which can be promoted in a suitably designed and sized pond/wetland system.

Based upon the “wetland” depth and large open water areas as shown in Figure 1, we consider it more appropriate to refer to the wetland treatment system as a ‘pond’, albeit with a wetland margin. We cannot see any flow optimisation apparatus in the photos supplied and assume there are not any (e.g. inlet flow distributors, bunds etc). Thus, this system will be prone to preferential flow paths, particularly during higher flow periods. This would further reduce the potential for interactions between wetland structures (e.g. plant stems) and inflowing landfill leachate.

Table 1: pH, total and dissolved iron and manganese concentrations in the wetland inflow and outflow in May and August 2019.

		Wetland inflow		Wetland outflow	
		10th May	1st August	10th May	1st August
pH		6.8	6.74	6.6	6.77
Total Iron (Fe)	(g/m^3)	6.3	4.4	6.7	3.7
Dissolved Iron (Fe)	(g/m^3)	0.05	0.8	3.1	0.29
Total Manganese (Mn)	(g/m^3)	2.4	2.2	2.5	2.2
Dissolved Manganese (Mn)	(g/m^3)	2.3	2.3	2.4	2.3
NH_4-N	(g/m^3)	1.52	1.30	1.58	1.30

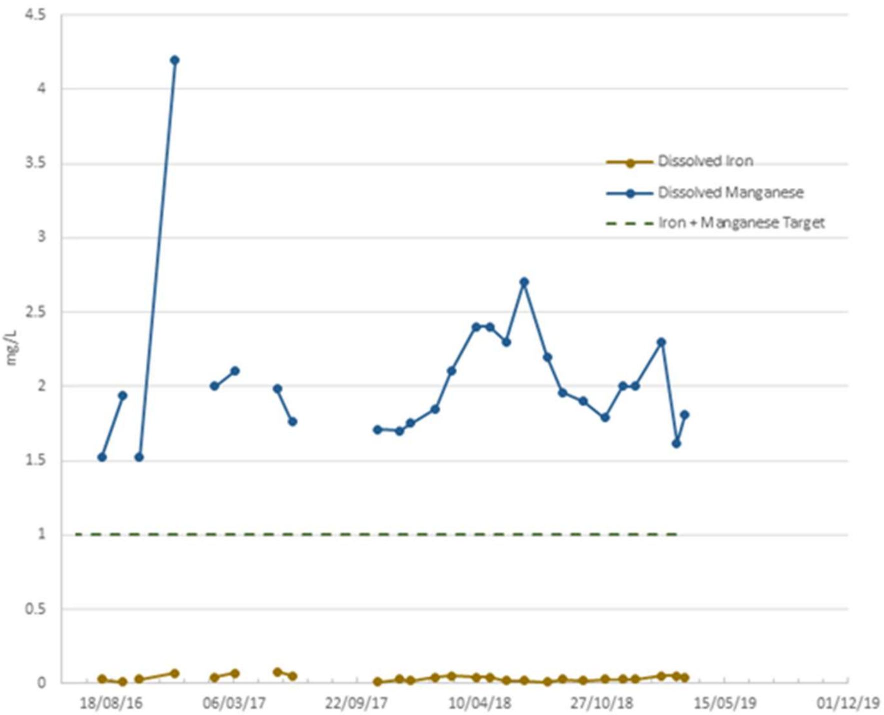

Figure 2: Dissolved Fe and Mn monitoring results (between June 2012 and July 2019) at the site 'TTD' located about 80 m below the wetland outlet

Issues and potential solutions to improve Fe and Mn removal

As described above, the main issues for the poor Fe and Mn removal include;

- Low pH (pH: < 7.0) and Dissolved Oxygen levels (~10% DO saturation) in the wetland limit abiotic oxidative processes for Fe and Mn removal,
- Deep wetland (water depths: 0.95-2.75 m) limit the growth of wetland plants and reduce surface for biofilm growth and adsorption surfaces for Fe and Mn removal, and
- Short detention time (12.2 h) and poor flow optimisation in the wetland will limit the precipitation of particulate (insoluble) Fe and (particularly) Mn salts.

'Aerobic' wetlands are considered to be a 'proven' technology for the treatment of landfill leachate and mine drainage waters for both Fe and Mn removal (Hedin et al. 1994a; Lesley et al. 2008; Park et al. 2008). For example, Lesley et al. (2008) reported that an aerobic treatment system combining an oxidation pond followed by horizontal-flow constructed wetlands consistently removed iron from 32 g/m^3 to effluent levels of below 1 g/m^3. The presence of wetland plants and substrate in the aerobic wetlands provided adsorption surfaces of filtration (and/or precipitation) for effective Fe removal, achieving an average areal removal rate of ~5.6 g/m^2/day. The wetland system also achieved about 76% Mn removal (from 1.5 to 0.4 g/m^3).

Lesley et al. (2008) considered microbial activities in wetland systems to be an important factor for Fe and Mn removal. Microorganisms in the wetlands are able to mediate the oxidation of iron, although biological oxidation of iron proceeds more slowly than abiotic oxidation. Adequate wetland plants are essential, as decomposition of fallen plant litter provides a food source (carbon) for bacterial communities which appear to be involved in bacterially-mediated removal of the metals (Lesley et al. 2008). Also plant photosynthesis (of emergent, or submerged macrophytes, or from free-floating microalgae) in wetlands or ponds not only supplies oxygen, but also temporarily increases the pH of the water. However, the short hydraulic detention time of this wetland (~12.2h) would prevent microalgal growth, and the water depth (0.95-2.75 m) over much of the wetland seems to exceed the depth for both emergent macrophytes and many submerged macrophytes[1]. In order for Mn removal to occur, the pH of the water would need to be raised sufficiently (pH: >8) for Mn (II) oxidation, converting it to insoluble Mn (IV), oxygen concentrations would likely need to increase, and retention times would need to substantially increase. Moreover, as the presence of iron has previously been shown to have an inhibitory effect on the removal of manganese and the formation of manganese oxides (Gouzinis et al. 1998), sufficient Fe removal should be achieved prior to the Mn removal.

Mitigation options

In order to achieve effective Fe removal, any mitigation measure will need to increase the D.O level of the leachate. For Mn removal, increases in both pH and D.O and providing absorption surfaces to remove colloidal manganese oxides are required. Thus, long-term management options include;

- Addition of an aeration system in the existing constructed wetland.
  - Active mechanical aeration would be the preferred option (e.g., installation of a mechanical surface aerator in the existing constructed wetland if electric power is accessible).
  - If mechanical aeration cannot be achieved in the existing wetland, then there may be benefits in constructing an aerated pond followed by a wetland in the proposed location.
- For Mn removal, elevated pH (>8) is required, along with increased retention time and provision of biological attachment surfaces.
  - Instead of installation of an open gravel-lined swale between the existing and proposed downstream wetland (as suggested by T&T Landfills), we would recommend using a lime chip filter to increase pH.
  - Alternatively, a chemical dosing system in the outlet of the existing wetland may be more reliable. Some neutralisation may be achieved in the downstream wetland, although to what degree is uncertain. Thus, a post-treatment neutralisation system may be required to minimise potential impacts of chronic and acute toxicity of Mn to aquatic life. (https://www2.gov.bc.ca/assets/gov/environment/air-land-water/water/waterquality/wqgs-wqos/approved-wqgs/manganese-or.pdf).
- Construction of the proposed downstream wetland treatment system <u>on its own</u> is unlikely to be effective. It should be noted that the existing wetland is currently ineffective for Fe and Mn removal. Thus, addition of a second wetland could only be recommended if addition of aeration or chemical dosing is undertaken, potentially in the existing wetland. If these conditions are met, we recommend use of experienced engineers or wetland specialists to achieve an appropriate design.

The addition of an aeration system will provide sufficient oxygen to promote both biotic and abiotic Fe/Mn oxidation. The recommended lime chip filter will provide attachment surfaces for Fe/Mn oxidising bacteria and adsorption surfaces for filtration as well as increasing the water pH.

Construction of the proposed downstream wetland as shown in Appendix 3 (e.g., horizontal flow constructed wetland vegetated with wetland plants (e.g., *Schoenoplectus* sp., *Carex* sp., and *Typha* sp.) and with a water depth of ~0.3-0.4 m will provide additional polishing treatment and moderate hydrological flow peaks which may affect the downstream environment.

It is worth noting that these solutions may permit Fe and Mn oxidation and settling in the wetland/pond, or in the channel below these systems. However, it has not permanently removed them. They will still be present in the system and may be released from the sediment when environmental conditions change (e.g., anoxic/anaerobic conditions). Consideration should be given to how these precipitated metals will be

[1] Only a few are visible in Figure 1.

managed in the long-term, either by capturing them in a properly designed and maintained sedimentation pond, with periodic removal and potentially dewatering.

References

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Appendix 1: Water quality testing results for inflow and outflow of the constructed wetland

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Certificate of Analysis

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Client:	Stantec New Zealand	**Lab No:**	2174475 SPv1
Contact:	A Fountain	**Date Received:**	10-May-2019
	C/- Stantec New Zealand	**Date Reported:**	15-May-2019
	PO Box 13052	**Quote No:**	79221
	Armagh	**Order No:**	
	Christchurch 8141	**Client Reference:**	T&T Landfill Monitoring 310001090
		Add. Client Ref:	Additional testing
		Submitted By:	Mr D Cameron

Sample Type: Aqueous

Sample Name:		WETLAND INFLOW 10-May-2019 2:20 pm	WETLAND OUTFLOW 10-May-2019 2:35 pm			
Lab Number:		2174475.1	2174475.2			
pH	pH Units	6.8	6.6	-	-	-
Total Alkalinity	g/m³ as $CaCO_3$	290	300	-	-	-
Total Hardness	g/m³ as $CaCO_3$	330	320	-	-	-
Electrical Conductivity (EC)	mS/m	85.2	84.9	-	-	-
Total Suspended Solids	g/m³	18	15	-	-	-
Dissolved Arsenic	g/m³	0.0015	0.0024	-	-	-
Total Arsenic	g/m³	0.0036	0.0035	-	-	-
Dissolved Calcium	g/m³	100	97	-	-	-
Dissolved Chromium	g/m³	0.0005	< 0.0005	-	-	-
Total Chromium	g/m³	0.00137	0.00097	-	-	-
Dissolved Copper	g/m³	< 0.0005	< 0.0005	-	-	-
Total Copper	g/m³	< 0.00053	< 0.00053	-	-	-
Dissolved Iron	g/m³	0.05	3.1	-	-	-
Total Iron	g/m³	6.3	6.7	-	-	-
Dissolved Lead	g/m³	< 0.00010	< 0.00010	-	-	-
Total Lead	g/m³	0.00039	0.00017	-	-	-
Dissolved Magnesium	g/m³	19.7	19.8	-	-	-
Dissolved Manganese	g/m³	2.3	2.4	-	-	-
Total Manganese	g/m³	2.4	2.5	-	-	-
Dissolved Zinc	g/m³	0.0018	< 0.0010	-	-	-
Total Zinc	g/m³	0.0032	0.0019	-	-	-
Total Ammoniacal-N	g/m³	1.52	1.58	-	-	-
Chemical Oxygen Demand (COD)	g O_2/m³	22	18	-	-	-
Dissolved Organic Carbon (DOC)	g/m³	4.8	13.2	-	-	-

Summary of Methods

The following table(s) gives a brief description of the methods used to conduct the analyses for this job. The detection limits given below are those attainable in a relatively clean matrix. Detection limits may be higher for individual samples should insufficient sample be available, or if the matrix requires that dilutions be performed during analysis.
Unless otherwise indicated, analyses were performed at Hill Laboratories, 28 Duke Street, Frankton, Hamilton 3204.

Sample Type: Aqueous

Test	Method Description	Default Detection Limit	Sample No
Filtration, Unpreserved	Sample filtration through 0.45µm membrane filter.	-	1-2
Total Digestion	Nitric acid digestion. APHA 3030 E (modified) 23rd ed. 2017.	-	1-2

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This Laboratory is accredited by International Accreditation New Zealand (IANZ), which represents New Zealand in the International Laboratory Accreditation Cooperation (ILAC). Through the ILAC Mutual Recognition Arrangement (ILAC-MRA) this accreditation is internationally recognised.
The tests reported herein have been performed in accordance with the terms of accreditation, with the exception of tests marked *, which are not accredited.

Appendix 2: Dissolved Oxygen wetland monitoring locations and results and water quality monitoring results on the 1st August 2019.

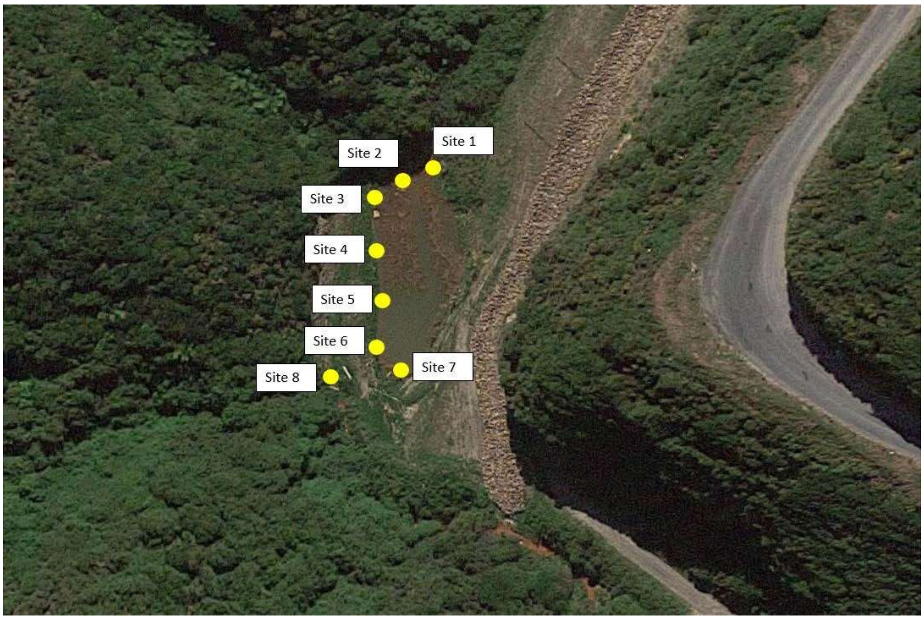

Figure 1: Wetland water quality sampling locations

Table 1: In-situ water quality results for sites around wetland 01 August 2019

Parameter/Site	1	2	3	4	5	6	7	8
pH	6.74	6.8	6.8	6.8	6.76	6.75	6.77	6.92
Temperature (°C)	14	13.9	13.9	13.8	13.7	13.7	13.9	13.8
DO (% sat)	5.8	4.9	7.6	9.8	11	11.6	6.6	56.4
DO (mg/l)	0.59	0.5	0.78	1.01	1.13	1.2	0.69	5.82
Conductivity SPC (mS/m)	102.7	102.6	102.4	102.1	101.6	101.5	101.9	101.6
Conductivity C (mS/m)	81.0	81.0	80.6	80.2	79.6	79.6	80.2	80.0

Table 2: Water quality wetland grab sample results

	Site 1	Site 1	Site 7	Site 8	Site 8
Parameter/ Date	10-May-2019	01-July-2019	01-July-2019	10-May-2019	01-July-2019
COD (g O_2/m^3)	22	15	15	18	16
DOC (g/m^3)	4.8	16.2	8.6	13.2	10.1
TSS (g/m^3)	18	6	8	15	13
pH	6.8	6.6	6.7	6.6	6.9
Total Alkalinity (g/m^3)	290	280	280	300	280
Electrical Conductivity (mS/m)	85.2	78.7	78.2	84.9	79.0
Total Iron (g/m^3)	6.3	4.4	3.7	6.7	3.8
Dissolved Iron (g/m^3)	0.05	0.80	0.29	3.1	0.06
Total Manganese (g/m^3)	2.4	2.2	2.2	2.5	2.3

Appendix 3: Proposed additional constructed wetland site and rock lined swale at the T & T landfill.