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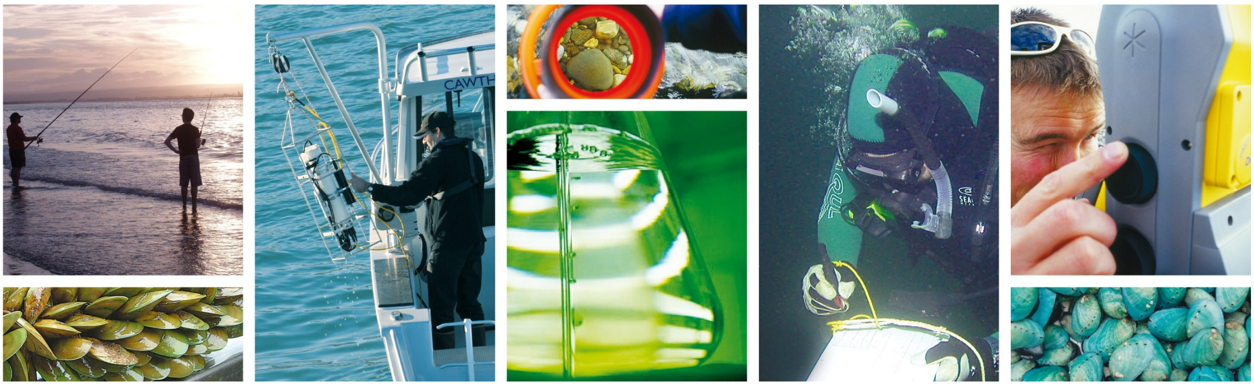
The Potential for Metal Contamination in the Maitai River



RESEARCH BASED SOLUTIONS

The Potential for Metal Contamination in the Maitai River

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Prepared for

NELSON CITY COUNCIL

(Envirolink 917-NLCC49)

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EXECUTIVE SUMMARY

Routine monitoring reports have shown that water with occasionally elevated manganese concentrations is discharged into the Maitai River from the Maitai Reservoir as part of the operation of the Nelson City water supply scheme. This review briefly summarises the current state of knowledge on manganese toxicity and the possible effects of elevated manganese levels in the Maitai River. In addition, consideration of other potentially co-occurring contaminants is also given.

There has been little research into the toxic effects of manganese in the aquatic environment and globally there is a variety of different upper-limit guidelines (ranging from 0.1 to 2.2 mg/L). The anoxic conditions present in the Maitai Reservoir hypolimnion during late summer-autumn produce the manganese (II) species that is soluble and more toxic to aquatic life. The levels of manganese discharged into the Maitai River (<1.2 mg/L during peak discharges) indicate only a moderate chance of direct or chronic toxicity to the river's aquatic life. However, there is a possibility that other metals, present in the metal-rich geology of the upper North Branch catchment, occur in the reservoir discharge at environmentally significant levels. Furthermore, moderately increased levels of manganese (and iron) in the reservoir's discharge may be encouraging the dominance of (potentially toxic) cyanobacterial communities over diatom-based communities in the Maitai River.

We make the following recommendations:

1) Full chemical analysis of the back-feed discharge should be conducted once a month over the course of a year and additional samples should be taken during discharges of anoxic water from the hypolimnion (generally February-May). Analysis of water from the North branch above the Reservoir and the South branch above the discharge site will help determine the natural background levels of potential contaminants.
2) To determine if the discharge is increasing the occurrence of undesirable algal species a survey and analysis of the algal communities around the discharge site is recommended.
3) An analysis of historical anoxic discharges volumes in relation to biomonitoring records may identify a correlation between the scheme's operating regime and the response of bio-indicators. This could be used to inform the future operation of the scheme.
4) Finally, if the above investigations conclude that discharges from the hypolimnion are having a negative impact on the Maitai River, we suggest analysing the ecological impacts (to both the reservoir and river) of replacing the discharge of deep-release anoxic water with water from intakes closer to the reservoir surface.

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1. INTRODUCTION

The Maitai River flows through Nelson city and is a significant recreational asset for the community. The river has important aesthetic values, frequented swimming holes and a trout fishery that (in the past) was ideally suited to junior anglers. In addition to these values, the Maitai Reservoir located in the upper catchment, is an important part of Nelson's municipal water supply.

Water with occasionally elevated manganese levels is discharged into the Maitai River from the Maitai Reservoir (Figure 4). Benthic macroinvertebrate and electric-fishing surveys have indicated a decline in water quality and juvenile trout numbers since 2002 (*e.g.* Olsen 2010) that may be linked to the manganese discharges. This review briefly summarises the current state of knowledge on manganese toxicity and assesses the risk that the Maitai Reservoir discharge may pose to aquatic life. Finally, consideration of other potentially co-occurring contaminants and recommendations for further investigation into the effects of the discharge is given.

1.1. Manganese as a toxicant

Manganese is a common element and is ubiquitously distributed throughout the earth's crust. As a contaminant it is considered relatively environmentally benign in comparison with other heavy metals such as lead, mercury or cadmium. Consequently, there has been little research into the toxic effects of manganese in the environment (Lasier *et al.* 2000; Howe *et al.* 2004; Baden & Eriksson 2006). However, if manganese is present in sufficient quantities it can induce iron deficiency in some algae (Csatorday 1984), interfere with the immune system and chemosensory organs in crustaceans (Baden & Eriksson 2006) and cause anaemia and internal haemorrhaging in fish (Stubblefield *et al.* 1997). In addition, many more subtle chronic effects have been demonstrated (Howe *et al.* 2004).

There is a wide range of suggested manganese concentrations amongst national guidelines to protect aquatic life. The "Australian and New Zealand Guidelines for Fresh and Marine Water Quality" (commonly known as the 'ANZECC guidelines') current trigger value is set at 1.2 mg/L which has a "moderate reliability" of protecting 95% of aquatic life. The toxicity of manganese is known to increase with increasing water hardness and this should be considered when setting guidelines (Howe *et al.* 2004). This has led to recommendations for more conservative upper limit manganese concentration guidelines. Howe *et al.* (2004) recommend a limit of 0.2 mg/L for soft waters using chronic effects estimates derived from acute LC_{50} data. Reimer (1999) recommends changes to British Colombia's manganese regulations to a sliding scale of between 0.6 to 1.9 mg/L depending on water hardness, according to this scale the safe manganese limit in the Maitai River could be around 0.8 mg/L. The South African aquaculture guidelines recommend that manganese levels do not exceed 0.1 mg/L to protect against possible chronic effects in fish (DWAFS 1996).

Common sources of toxic manganese levels in the environment include sewage discharges, acid mine leachates, sediment-pore water and hypolimnetic reservoir releases (Howe *et al.* 2004). The latter is of specific interest in this report. Under aerobic conditions, with near neutral pH, dissolved manganese concentrations tend to be low, as equilibrium reactions favour manganese species that readily form insoluble oxides. However, under anaerobic conditions redox reactions produce the manganese(II) species (Mn^{++}) that is soluble and more toxic to aquatic life (Wetzel 1983). Concentrations of manganese in waters of near pristine catchments range from 0.001 to 10.0 mg/L but it is uncommon for concentrations to exceed 0.2 mg/L (Howe *et al.* 2004). Hypolimnetic reservoir release water may contain manganese levels of 1 to 2 mg/L (Nix & Ingols 1981). The oxidation process of manganese (II) is relatively slow and, as a consequence, manganese may remain in a form that is harmful to aquatic life for a considerable period in aerobic conditions (approximately three days in pH-neutral conditions) (Wetzel 1983). The backfeed discharge is approximately 16 km upstream from where the Maitai River enters the Nelson Haven. Average water velocities in the Maitai River in excess of 0.06 m/s would mean that water from the backfeed discharge would reach the Nelson Haven within three days. Average velocities in the Maitai River are extremely likely to exceed 0.06 m/s. Therefore, harmful forms of manganese present in the backfeed discharge are likely to affect the entire length of the Maitai River before they are oxidised and incorporated into the sediments in less toxic forms.

Table 1. LC$_{50}$ (Lethal concentration for 50% of test subjects) and EC$_{50}$ (Effective concentration for 50% of test subjects) results for freshwater animals. Table modified from IPCS (International Programme of Chemical Safety) manganese report, for original references see (Howe *et al.* 2004).

Organism	End-point	Manganese concentration (mg/litre)	Reference
Freshwater Algae			
Alga (*Scenedesmus quadricauda)*	12-day EC$_{50}$ (growth inhibition)	5	Fargašová *et al.* (1999)
	12-day EC$_{50}$ (total chlorophyll reduction)	1.9	Fargašová *et al.* (1999)
Alga (*Pseudokirchneriella subcapitata*)	72-h EC$_{50}$ (growth inhibition) 1	8.3	Reimer (1999)
	4-day EC$_{50}$ (total cell volume reduction)	3.1	Christensen *et al.* (1979)
Freshwater Invertebrates			
Sludge worm (*Tubifex tubifex*)	48-h LC$_{50}$	208.1	Khangarot (1991)
	96-h LC$_{50}$	170.6	Khangarot (1991)
	48-h LC$_{50}$	171.4–350.2	Rathore & Khangarot (2002)
	96-h LC$_{50}$	164.6–275.7	Rathore & Khangarot (2002)
Daphnid (*Daphnia magna*)	48-h LC$_{50}$	9.8	Biesinger & Christensen (1972)
	21-day LC$_{50}$	5.7	Biesinger & Christensen (1972)
	48-h EC$_{50}$ (immobilisation)	8.3	Khangarot & Ray (1989)
	48-h LC$_{50}$	0.8–76.3	Reimer (1999)
	48-h EC$_{50}$ (immobilisation)	4.7–56.1	Baird *et al.* (1991)
	48-h EC$_{50}$ (immobilisation)	2.0	Sheedy *et al.* (1991)
	48-h EC$_{50}$ (immobilisation)	40	Bowmer *et al.* (1998)
Amphipod (*Hyalella azteca*)	96-h LC$_{50}$	3.6–31	Reimer (1999)
	96-h LC$_{50}$	3.0–13.7	Lasier *et al.* (2000)
Amphipod (*Crangonyx pseudogracilis*)	48-h LC$_{50}$	1389	Martin & Holdich (1986)
	96-h LC$_{50}$	694	Martin & Holdich (1986)
Midge (*Chironomus tentans*)	96-h LC$_{50}$	5.8–94.3	Reimer (1999)
Freshwater fish			
Rainbow trout (*Oncorhynchus mykiss*)	96-h LC$_{50}$	4.8	Davies & Brinkman (1994)
	28-day LC$_{50}$ (embryo-larval test)	2.9	Birge (1978)
Brown trout (*Salmo trutta*)	96-h LC$_{50}$	3.8–49.9	Davies & Brinkman (1994, 1995)
Coho salmon (*Oncorhynchus kisutch*)	96-h LC$_{50}$	2.4–17.4	Reimer (1999)
Goldfish (*Carassius auratus*)	7-day LC$_{50}$ (embryo-larval test)	8.2	Birge (1978)
Indian catfish (*Heteropneustes fossilis*)	96-h LC$_{50}$ Cl2	3350	Garg *et al.* (1989b)

2. MANGANESE IN THE MAITAI

2.1. Maitai Reservoir limnetic conditions

The Maitai Reservoir scheme has been operational since 1987. Under normal flow conditions, water is abstracted directly from the South Branch of the Maitai River at the intake weir and this water is replaced by water from Maitai reservoir (termed the 'Backfeed') which is discharged at the foot of the intake weir (Figure 1). The consent conditions relevant to the scheme's operation can be found in Stark & Hayes (1996).

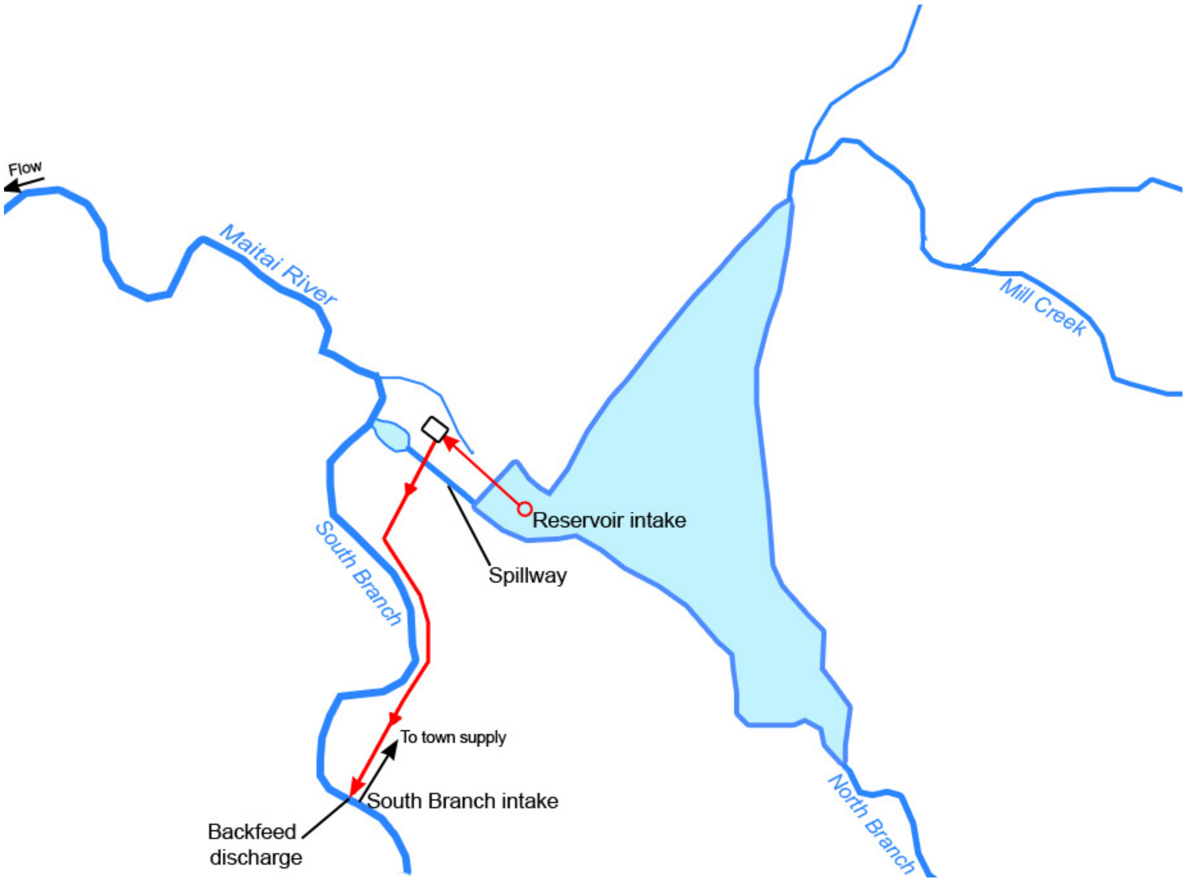

Figure 1. Diagram of the Maitai Water Supply Scheme with the water supply intake (labelled 'South Branch intake') and backfeed shown.

Since its construction, there has been a consistent pattern of late summer thermal stratification in the lower levels of the reservoir (*e.g.* Figure 2). The reservoir water that is discharged to the South Branch from the backfeed is usually extracted from the lowest intake (Intake 3, Scour) in the Reservoir, which from January until turn-over (break-up of stratification) in April-May, can be anoxic or near-anoxic (*e.g.* Figure 3). Abstracting water from deep within the reservoir ensures that resource consents for maintaining near-natural river temperatures are complied with but increases the risk of discharging water with high levels of contaminants such as manganese (II). The highest manganese level in the dam's hypolimnion was recorded in March 2006 (1.7 mg/L) (Olsen 2006).

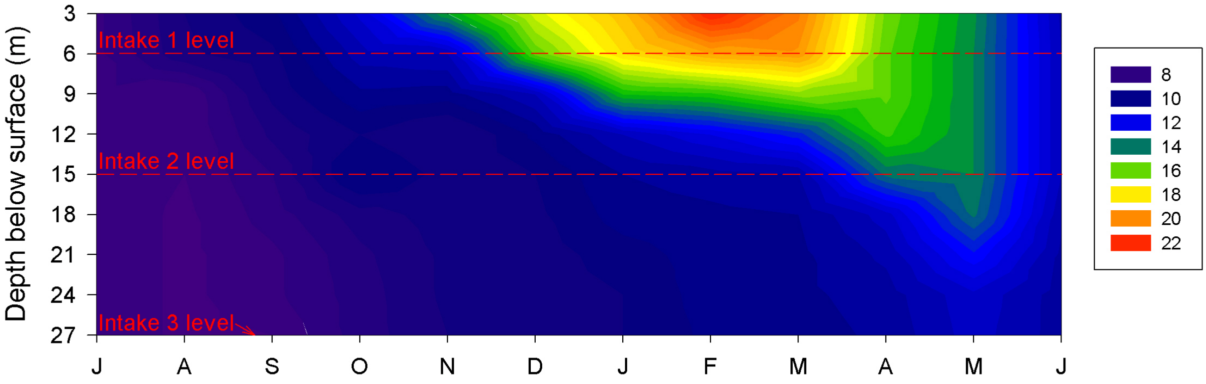

Figure 2. Temperature (°C) through the water column in Maitai Reservoir (below the level 3 m below the spillway level) during 2009-2010. Contours based on twelve monthly measurements at nine depths. Figure from Olsen (2010).

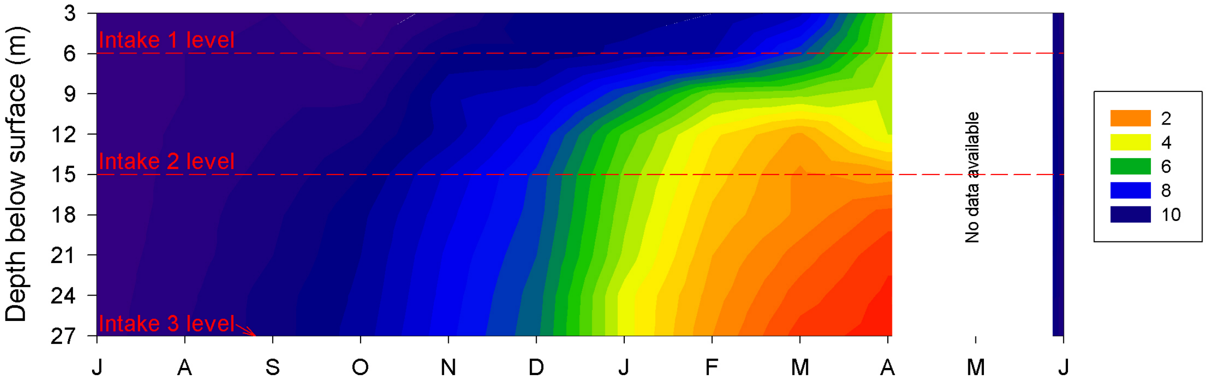

Figure 3. Dissolved oxygen concentration (g m^{-3}) through the water column in Maitai Reservoir (below the level 3 m below the spillway level) during 2009-2010. Contours based on twelve monthly measurements at nine depths. No data was available in May 2010 due to a probe malfunction. Figure from Olsen (2010).

2.2. Risk of increased manganese in the Maitai River

Elevated levels of manganese in the Maitai Reservoir discharge have the potential to reduce galaxiid, eel and brown trout populations in the Maitai River. The consented manganese level for the Maitai River is currently set at 1 mg/L. This has been breached on two occasions during the history of the reservoir (March 2006, May 2007) (Figure 4). However, peak concentrations in the South Branch approximately 900 m downstream of the discharge have been below 0.5 mg/L during most years (Figure 4). Nevertheless, given that little is known about chronic manganese toxicity, it is possible that harmful levels of manganese may be lower than the current consented concentration.

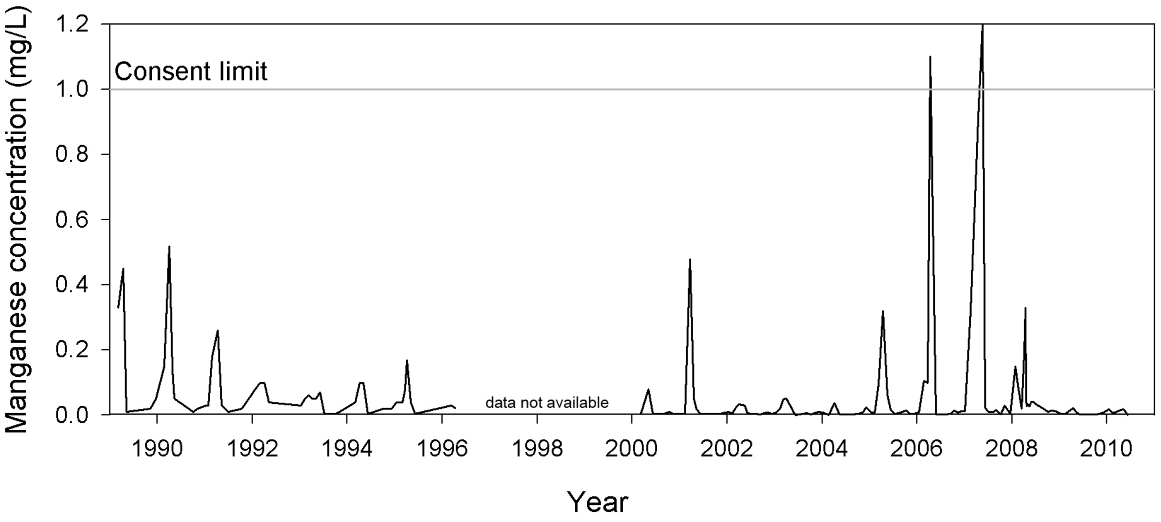

Figure 4. Concentration of Manganese at Site B (approximately 900 m downstream of the backfeed discharge) in the South Branch of the Maitai River from 1989 to 2010. No data was available between April 1996 and January 2000.

Manganese (and iron) levels can also affect the composition and biomass of freshwater algal communities (Wetzel 1983). Algal communities have a significant influence on the rivers ecology and can impact upon aesthetic and recreational values. For instance, filamentous growths can detract from a swimming experience and the proliferation toxic cyanobacteria is a potential public health issue.

2.2.1. *Manganese toxicity and limitation in algal communities*

There is a wide range of tolerance values to manganese amongst freshwater algae. The most sensitive freshwater species potentially being the diatom *Scenedesmus quadricauda* (toxicity data is summarised in Table 1). High concentrations of manganese (>1 mg/L) have been shown to inhibit blue green and green lake algae (Gerloff & Skoog 1957). In addition, low concentrations of <0.05 mg/L can retard the growth of cyanobacteria and favour diatom-dominated algal communities in streams (Wetzel 1983). The moderately increased manganese levels in the Maitai River (0.1 to 0.5 mg/L during most years' peak discharges) may have a fertilising effect on the river and provide a favourable environment for the growth of cyanobacteria. A RAM 1 algal assessment (Rapid Algal Assessment Protocol) conducted during July 2010 showed that periphyton coverage at Site B (below the discharge) was more than twice that of the control site above the discharge (60.4% versus 26.0%) with the downstream site dominated by cyanobacteria mats. Furthermore, only 4% of quadrats at Site B lacked visible periphyton, compared with 11% at the control site. The toxic algal species *Phormidium* was present at both sites and it is likely that this species dominated the periphyton cover at Site B (Olsen 2010). Limited nutrient data suggests that two sites have similar nitrogen/phosphorus levels (unpublished data collected on June and July 2010), hydrological histories and physical characteristics. Therefore, micronutrients (most likely manganese or iron) present in the reservoir discharge may be causing the increased algal growth at Site B.

2.2.2. Manganese toxicity in freshwater invertebrates

There is a wide range of sensitivity to manganese in invertebrates. Toxic effects for *Daphnia magna* occur at 0.8 mg/L and *Crangonyx pseudogracilis* can tolerate up to 1389 mg/L. Tolerance levels are summarised in Table 1. To my knowledge there has been no direct toxicity work on the effects of manganese on New Zealand native macroinvertebrates. Therefore, there is a chance that the elevated manganese levels in the Maitai River could cause toxic effects in some native invertebrates. Furthermore, if increased manganese encourages the growth of cyanobacteria this could alter the invertebrate communities and increase the relative numbers of chironomids (which are typically low-scoring taxa in macroinvertebrate indices). There are numerous correlative studies that report low or declining macroinvertebrate indices in streams affected by mine runoffs and hypoxic reservoir discharges which contain high levels of manganese. However, these studies cannot separate the effects of co-occurring contaminants or physical stressors that occur in these environments. Nevertheless, elevated Manganese (and iron) levels could be a good indicator of hypolimnetic water that is likely to negatively impact upon macroinvertebrate communities (Scullion *et al.* 1982; Brittain & Saltveit 1989). In contrast, one overseas study found that macroinvertebrate health indices increased with increasing manganese concentrations (up to 0.6mg/L) in unregulated streams (Hirst *et al.* 2002). The limited information that is available suggests that stream invertebrates should be able to tolerate manganese levels present in the Maitai River below the discharge (Howe *et al.* 2004).

2.2.3. Manganese toxicity in fish

There appears to be no direct research into the acute or chronic manganese tolerance levels for New Zealand native fish. Manganese acute toxicity values in fish range from 2.4 mg/L for Coho salmon (*Oncorhynchus kisutch*) to 3350 mg/L for the Indian catfish (*Heteropneustes fossilis*) (Table 1). To protect against chronic effects in fish, conservative estimates of safe concentrations (derived from acute toxicity values) range from 0.1–2.2 mg/L, dependent on fish species and water hardness (DWAFS 1996; Stubblefield *et al.* 1997; Howe *et al.* 2004). Correlative studies have linked high manganese levels in deepwater reservoir discharges with declining fish health (Grizzle 1981). Rainbow trout deaths in a hatchery that sourced water from the hypolimnion of a reservoir were correlated with increased manganese concentrations of between 0.5 and 1 mg/L (Nix & Ingols 1981). The authors concluded that although this was just a correlative study, elevated manganese levels (>0.5 mg/L) could be a good indicator of the toxicity of hypolimnetic water to fish.

Brown trout are the only species present in the Maitai River that have been specifically tested for manganese toxicity. They appear somewhat more tolerant than rainbow trout with no observable effect at concentrations of 3.8 mg/L (Table 1). Stubblefield *et al.* (1997) report no observable chronic effect in early life stage tests at concentrations between 4.47 mg/L to 8.68 mg/L (depending on water hardness). This would suggest that brown trout in the Maitai River should tolerate the levels present in the release water from the reservoir. However, it is possible an increased toxic effect of manganese occurs when present in combination with other contaminants or stress-inducing conditions (Grizzle 1981). Thus chronic effects could occur at significantly lower levels than those determined by standard toxicity testing.

2.3. Other potential contaminants from the Maitai Reservoir

The upper Maitai catchment drains a section of the Dun Mountain Ophiolite belt. This unique geology means that naturally high levels of metals, such as nickel and chromium (the latter being significantly more toxic) may occur in the Maitai River (Sano *et al.* 1997). The speciation of a range of heavy metals to soluble and more toxic forms can occur under anoxic conditions, such as those present in the Maitai Reservoir hypolimnion (Wetzel 1983). Together with the elevated manganese and iron levels there could be a combination of heavy metals present in higher than background concentrations in the hypolimnion. Indeed, the apparent ecological effects of the discharge on the Maitai River may be due to a mixture of contaminants causing a multiple stress effect on the river. Complex interactions between different contaminants and physical stressors may increase or decrease the toxicity of the different substances (Vinebrooke *et al.* 2004). For example, the toxicity of both manganese and DDT to freshwater invertebrates was increased when the two contaminants co-occurred (Mejia-Saavedra *et al.* 2005). Conversely, the presence of manganese has been shown to ameliorate the toxicity of other metals such as cadmium and zinc to micro-algae (Sunda & Huntsman 1998). Further investigation into the possible presence and concentrations of other metals in the Maitai Reservoir discharge is required before the possibility of heavy metal contamination can be ruled out.

2.4. Conclusions and recommendations

Anecdotal reports of declining fishery value, unsightly “rust” deposits and increased algal growths have raised public concern over the discharge from the Maitai Reservoir. This has prompted previous investigations into anthropogenic influences on the Maitai River (Crowe *et al.* 2004). However, these reports have generally focused on temperature and flow conditions set out in the resource consents for the scheme’s operation. The levels of manganese discharged into the Maitai River (<1.2 mg/L and commonly below 0.5 mg/L during peak discharges) suggest that there is only a moderate possibility of direct or chronic manganese toxicity to various components of the river’s aquatic life (although it must be noted that manganese toxicity data on native species is inadequate). Nevertheless, fertilising the river with moderate levels of bio-available manganese (and iron) from the reservoir’s anoxic zone may be encouraging the growth of cyanobacteria. This could have significant flow-on effects for invertebrate and fish communities in the river, and encouraging the growth of toxic cyanobacteria species such as *Phormidium* may represent a public heath concern.

The potential risk of other co-occurring contaminants discharged into the Maitai River from the reservoir's hypolimnion is unknown. Part of the Maitai River (North branch) drains the Dun Mountain mineral belt. Naturally high levels of certain metals (principally nickel and chromium) are present in this geology and could be supplied to the lake via sediment and organic matter from the North branch of the river. These metals may be altered into more soluble and toxic forms in the anoxic conditions of the reservoir's hypolimnion during late summer and then discharged into the Maitai River via the deep water intake. It appears that this issue has largely been overlooked as a potential cause of the apparent decline in the river's health. Any metals in the reservoir are likely to remain in the anoxic layer or be rapidly precipitated into the lake sediments during autumn de-stratification. Therefore, there is potential to reduce the contaminant load in the Maitai River by discharging from the warmer, oxygenated surface waters during late summer lake stratification. However, this may result in the current temperature conditions in the river being breached and cause contaminants or nutrients to build up in the anoxic layer of the lake. Nevertheless, warm/low-contaminant discharges may be less environmentally damaging than cool/high-contaminant discharges from the hypolimnion. Analysing the ecological consequences of reducing the relative volume of anoxic water in the discharge may help devise an operating regime that improves the overall health of the river.

2.4.1. Recommendations

Based on the review of the existing data and literature on manganese toxicity, we recommend the following:

1) Full chemical analysis of the backfeed discharge should be conducted once a month over the course of a year and additional samples should be taken specifically during discharges of anoxic water from the hypolimnion (generally February-May). Analysis of water from the North branch above the Reservoir and the South branch above the discharge site will help determine the natural background levels of potential contaminants.
2) More intensive surveys of the algal communities above and below the discharge and a chemical analysis of algal cells may help determine if chemical constituents present in the discharge are contributing to undesirable algal growths.
3) A desk-top analysis of historical discharge volumes and biomonitoring records may identify if a correlation exists between the scheme's operating regime and the declining trend in macroinvertebrate community indices (which commenced around 2001-2002; Olsen 2010). This could be used to inform how the scheme can be operated in the future to minimise its ecological impact.
4) If a problem with metal contamination is identified, modeling of physical and chemical profiles within the lake under different operating regimes would allow assessment of mitigation options. Any investigation of changes in the scheme's operation will have to

consider both the long-term water-quality of the lake and the ecological consequences in the river.

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