Environment Canterbury Regional Council
Kaunihera Taiao ki Waitaha

Science Advice

Date	5 August 2022
To	Tim Davie *(Director, Science)*
CC	Catherine Schache *(General Counsel)*
From	Carlos Rosado *(Senior Groundwater Scientist)*; Shirley Hayward *(Science Team Leader – Water Quality and Ecology)*; Michael Massey *(Principal Science Advisor – Contaminated Land)*

Summary of Science investigation of elevated manganese in Timaru District Council's Opihi water intake

The scope of this advice note is to document Environment Canterbury's findings related to river and groundwater sampling around the Opihi water supply intake.

Key Points

- No anthropogenic sources of manganese were identified (i.e., dumping of manganese-containing substances). Naturally-occurring manganese likely was mobilised from aquifer sediments into groundwater, which then made its way to the Opihi intake gallery.
- Organic matter in groundwater can cause naturally-occurring microbial activity to decrease dissolved oxygen in the groundwater and release trace elements like manganese from aquifer sediments.
- Removing sources of organic matter slows microbial activity and decreases the release of manganese from aquifer sediments.
- In addition to elevated manganese, other measured water quality parameters (low dissolved oxygen, low nitrate, elevated ammonium, elevated iron and trace elements) suggest organic matter as a contributing factor for the observed manganese concentrations.
- A silage storage area located approximately 500 m upgradient from the Opihi intake gallery was identified as a potential contributor of organic matter, in the form of silage leachate that might have seeped into the shallow groundwater.
- Because there are a number of possible contributors of organic matter, we were unable to confirm that the silage was the only likely source of organic matter in this area. Groundwater quality improved after the removal of the silage, including increased dissolved oxygen, decreased manganese, and decreased iron. We therefore consider it likely that silage leachate contributed to elevated manganese in groundwater upgradient of the Opihi intake gallery.

Introduction

Following reports of discolouration of water in Timaru in December 2021, Timaru District Council (TDC) established that elevated concentrations of manganese in the Opihi water supply intake gallery caused the orange discoloration. The Opihi intake draws water from one double-branch gallery located on the north bank of the Opihi River, west of Waitohi Pleasant Point Road. One of the branches of the gallery is located close to the Opihi River, running parallel to the river flow, and is generally considered to be drawing recent river water. The other branch is positioned perpendicular to the river and draws from shallow groundwater (Figure 1).

To assist TDC in understanding the causes of elevated manganese concentrations in their water supply, Environment Canterbury (ECan) undertook sampling of river water and groundwater in the vicinity of the intake. This report documents the results of ECan sampling and analysis.

Previous sampling (2020)

Groundwater samples were collected from a selection of shallow wells in and around the Pleasant Point area in 2020 to examine the state of groundwater quality in the area, since limited previous groundwater quality data were available. Two rounds of samples were collected, in August and November 2020. The sampling included the Opihi intake gallery and a number of upgradient wells located on both sides of the Opihi River. Results for dissolved manganese did not indicate any concentrations of concern at these sites. At the Opihi intake gallery, manganese was not detected in the August samples, and in November it was found at a concentration of 0.0006 mg/L, just above the laboratory detection limit. The highest manganese result was observed in a well located 870 m upgradient from the Opihi intake gallery, at a concentration of 0.01 mg/L, which is below the New Zealand drinking water aesthetic standard (0.04 mg/L for staining of laundry) and health-based standard (0.4 mg/L). These results suggest that manganese contamination was not an issue at the Opihi intake gallery and in the upgradient shallow groundwater in late 2020.

Recent sampling (2022)

In mid-December of 2021, TDC received numerous complaints regarding discoloured drinking water. Sampling of groundwater wells was undertaken by TDC in January 2022 and found that elevated manganese was present in water from the Opihi intake gallery. ECan scientists (including the authors) were asked to advise on potential reasons for the increased manganese concentrations.

Samples of river water and deposited fine sediment were collected from five sites on the Opihi and Opuha rivers on 19th January 2022. Samples were sent to Hill Laboratories for analysis of total metals (manganese, iron, arsenic, cadmium, chromium, copper, lead, nickel and zinc).

On 25th January 2022, after discussions with TDC, ECan also sampled several wells in the area, on both sides of the Opihi River, as far as ~10 km upriver.

We analysed groundwater samples for a broad suite of parameters (not only manganese). Low dissolved oxygen, detections of ammonium and elevated concentrations of dissolved organic carbon were measured, together with elevated concentrations of manganese, iron, and arsenic at one TDC monitoring well in the shallow groundwater upgradient from the Opihi intake gallery. Water from the gallery itself had only slightly elevated manganese. We considered it possible that organic matter in groundwater could have created low-oxygen conditions that resulted in the release of trace elements (such as manganese, arsenic, and iron) from aquifer sediments. A recent ECan Science Report (Pearson et al., 2022) presents a region-wide perspective of these processes in Canterbury groundwater.

Bore logs from wells drilled on both sides of the Opihi River showed that layers of “blue clay” are present in the subsurface. “Blue clay” is indicative of the presence of buried sources of natural organic matter, such as peat lenses. The blue colouration is from low-oxygen conditions, due to the presence of reduced iron (which has a grey or bluish colour), as opposed to oxidised iron (which has a reddish or yellowish colour). The presence of “blue clay” suggests that natural sources of organic matter exist in the nearby aquifer sediments, but it was unclear whether natural sources of organic matter by themselves, or in concert with other natural changes, could have caused the observed elevated manganese concentrations.

A silage storage area located approximately 500 m upgradient from the Opihi intake gallery was identified as a potential contributor of organic matter, in the form of silage leachate that might have seeped into the shallow groundwater. Silage is fermented grain and/or grass used for animal feed, and the fermentation process produces leachate rich in organic matter and nutrients. After consultation with ECan scientists and the landowner, TDC installed provisional groundwater monitoring wells up- and downgradient from the silage storage area to examine whether it might contribute to elevated manganese concentrations in groundwater. Subsequently, from March to June 2022 ECan conducted a groundwater quality monitoring programme of the TDC monitoring wells to determine if there were changes in groundwater quality before or after silage removal.

Additionally, ECan staff from the Contaminated Land and Waste team attended the silage storage site in April 2022 (during removal of silage) and identified no apparent issues associated with trace metal discharge to the land surface.

Data, analysis, and interpretation

The results of river water and river fine sediments are presented in Table 1 and Table 2. Key findings from the analysis of the Opihi River water and sediment samples were:

- Metals were detected in some water samples, but none were found at levels above maximum acceptable values (MAVs) from the drinking water standards, or above thresholds of concern for aquatic ecosystems.
- Slightly higher manganese and iron concentrations found in the sediment samples just downstream of Lake Opuha are to be expected given the history of deoxygenated waters at times in the lake (resulting in release of manganese and iron into the water column), but the results did not indicate that there is either localised or widespread excessive manganese in the river system.
- Other metal concentrations did not indicate any unnatural sources or concerns, and were well below guidelines for protecting ecosystem health.

From March to June 2022, ECan collected weekly samples from eight shallow monitoring wells, two upgradient and six downgradient, from the silage storage area (Figure 1, Table 3).

At the start of the groundwater quality monitoring programme in March, water sampling showed elevated concentrations of manganese, arsenic, and iron, and low dissolved oxygen and nitrate in some monitoring wells located downgradient from the silage storage area. Detectable concentrations of manganese and iron were also observed in the two upgradient monitoring wells, but at lower concentrations than in the downgradient wells. The results are presented in Figure 2 (monitoring wells upgradient from the silage storage area) and Figure 3 (monitoring wells downgradient from the silage storage area). In the groundwater samples from mid- to late March, we note that in some monitoring wells, manganese concentrations started to decrease before silage removal. This initial decrease might have been due to dilution caused by rainfall recharge [1].

By late April, when silage removal was well underway, concentrations of manganese, iron and arsenic decreased, and dissolved oxygen increased in all monitoring wells. In some wells, the concentrations changed rapidly, while in others the decrease was more gradual. The groundwater quality continued to improve through May and June, with only one downgradient monitoring well (BZ19/0332) still having concentrations of manganese above the health-based drinking-water value of 0.4 mg/L. However, the consistent decreasing trend for manganese in this well suggests that the concentrations will continue to decrease (see manganese graph for BZ19/0332 in Figure 3).

These results indicate that the silage leachate was a likely contributor to the observed decrease in dissolved oxygen, and resulting increases in manganese, arsenic, and iron.

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[1] The nearest ECan rainfall sites at Kakahu Bush and Hadlow recorded more than 20 mm of rainfall in mid- and late March 2022.

However, the two wells upgradient of the silage storage area (BZ19/0334 and BZ19/0335) also had low dissolved oxygen and elevated concentrations of iron and manganese, which changed over the sampling period. It is unclear whether the silage storage area had impacted groundwater in these upgradient wells, or if there might have been other source(s) of organic matter.

Overall, the groundwater sampling data shows decreasing concentrations of manganese, iron, and arsenic, and increasing dissolved oxygen, in all monitoring wells over the sampling period. In wells with < 1 mg/L dissolved oxygen as at June 2022 (wells BZ19/0332, BZ19/0336, and BZ19/0337), we consider that chemical reactions between dissolved iron and dissolved oxygen might be slowing the rate of dissolved oxygen increase. Alternatively, there might be organic matter (e.g., residual silage leachate, or organic matter from other sources) causing localised effects. Manganese concentrations might therefore remain elevated in these wells for some time. Nonetheless, groundwater quality is improving in the area upgradient from the Opihi intake gallery, and it is expected that groundwater quality will continue to improve as dissolved oxygen increases.

References

Pearson, A., Scott, L., Wilkins, B. 2022. Arsenic and manganese in Canterbury groundwater: occurrence, sources, and mechanisms. Environment Canterbury Report No. R22/06.

Attachments: Appendix 1; *(full dataset available upon request)*, Appendix 2 – Peer review.

File reference: (Content Manager: WATE/INGW/QUAL/INVE)

Appendix 1

Table 1: *Results of river water samples collected from Opihi catchment on 19th January 2022.*

Water sample results	Units	Detection limit	Downstream of Lake Opuha Dam	Opuha River at Skipton Bridge	Opihi River upstream of TDC Intake	Opihi Lagoon Milford Huts	Opihi Lagoon Penny Lane
Site co-ordinates		NZTM easting	1431368	1438180	1451067	1468105	1468026
		NZTM northing	5124969	5117204	5099227	5096022	5095636
Metals							
Total Iron	g/m^3	0.021	0.102	0.066	ND	ND	0.23
Total Manganese	g/m^3	0.00053	0.03	0.0075	0.00136	0.0106	0.021
Total Arsenic	g/m^3	0.011	0.0011	ND	ND	ND	ND
Total Cadmium	g/m^3	0.00053	ND	ND	ND	ND	ND
Total Chromium	g/m^3	0.0053	ND	ND	ND	ND	ND
Total Copper	g/m^3	0.0053	0.00115	0.00094	0.00083	ND	0.00075
Total Lead	g/m^3	0.0011	ND	ND	ND	ND	0.00015
Total Nickel	g/m^3	0.0053	ND	ND	ND	ND	ND
Total Zinc	g/m^3	0.011	ND	ND	ND	ND	ND

ND = not detected above laboratory detection limit.

Table 2: *Results of analysis of deposited fine sediment samples collected from Opihi catchment on*

Sediment sample results Metals	Units	Detection limit	Downstream of Lake Opuha Dam	Opuha River at Skipton Bridge	Opihi River upstream of TDC Intake	Opihi Lagoon Milford Huts	Opihi Lagoon Penny Lane
Total Recoverable Iron	mg/kg dry wt	0.010 - 0.8	22,000	22,000	16,200	20,000	18,600
Total Recoverable Manganese	mg/kg dry wt	0.010 - 0.8	580	450	270	330	290
Total Recoverable Arsenic	mg/kg dry wt	0.010 - 0.8	3.5	2.7	1.9	2.9	2.8
Total Recoverable Cadmium	mg/kg dry wt	0.010 - 0.8	0.097	0.048	0.024	0.055	0.043
Total Recoverable Chromium	mg/kg dry wt	0.010 - 0.8	14.7	12.9	9.3	11.9	10.9
Total Recoverable Copper	mg/kg dry wt	0.010 - 0.8	11.7	10.2	6.6	10.4	8.8
TotalRecoverable Lead	mg/kg dry wt	0.010 - 0.8	15.3	10.1	6.4	10.9	9.1
Total Recoverable Nickel	mg/kg dry wt	0.010 - 0.8	9.1	9	8.1	9.3	8.7
Total Recoverable Zinc	mg/kg dry wt	0.010 - 0.8	64	51	34	47	42

Table 3: *Monitoring wells sampled by ECan from March to June 2022.*

No.	TDC well name/number	ECan well number	Location in relation to silage storage area	Well depth (m)
1	Bore A	BZ19/0334	Upgradient	3.6
2	Bore B	BZ19/0335	Upgradient	3
3	Bore C	BZ19/0336	Downgradient	3.7
4	Bore D	BZ19/0337	Downgradient	3.3
5	Bore E	BZ19/0338	Downgradient	3.1
6	Bore F	BZ19/0339	Downgradient	2.7
7	Bore 4	BZ19/0330	Downgradient	4
8	Bore 6	BZ19/0332	Downgradient	4

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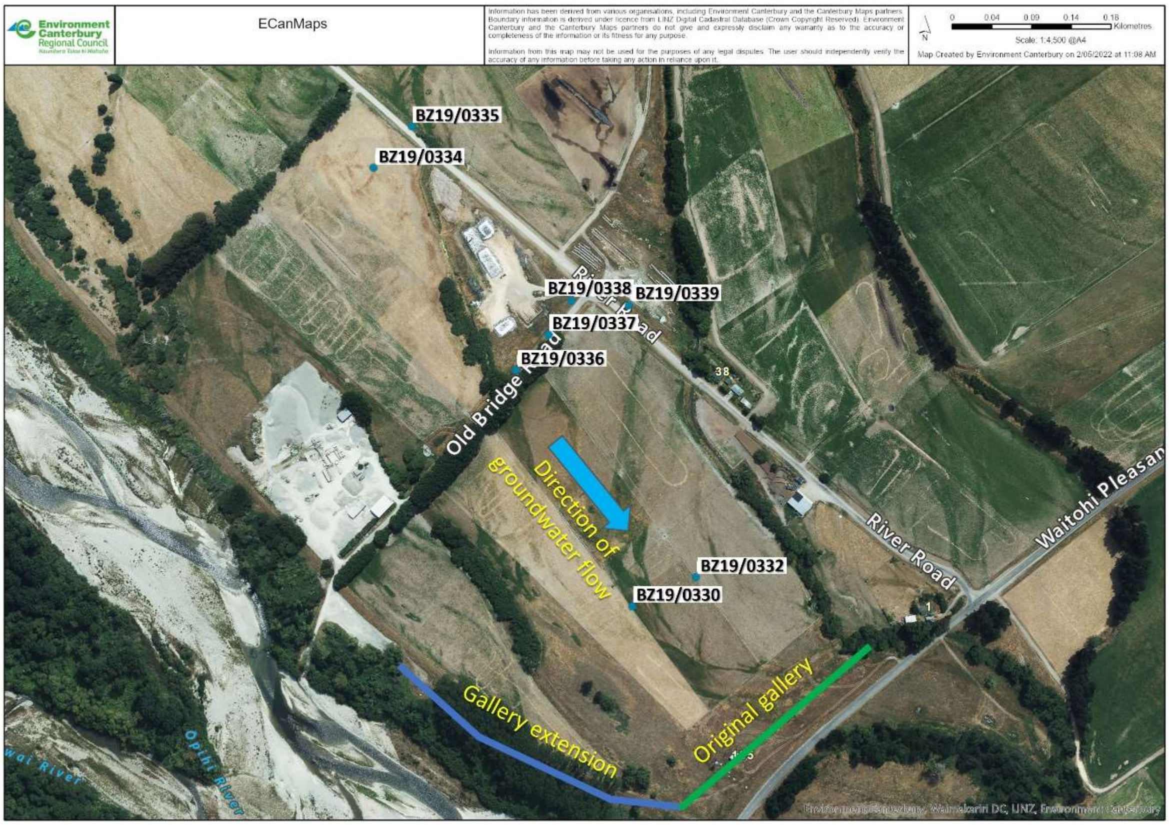


Figure 1: *Location of monitoring wells and Opihi intake gallery.*

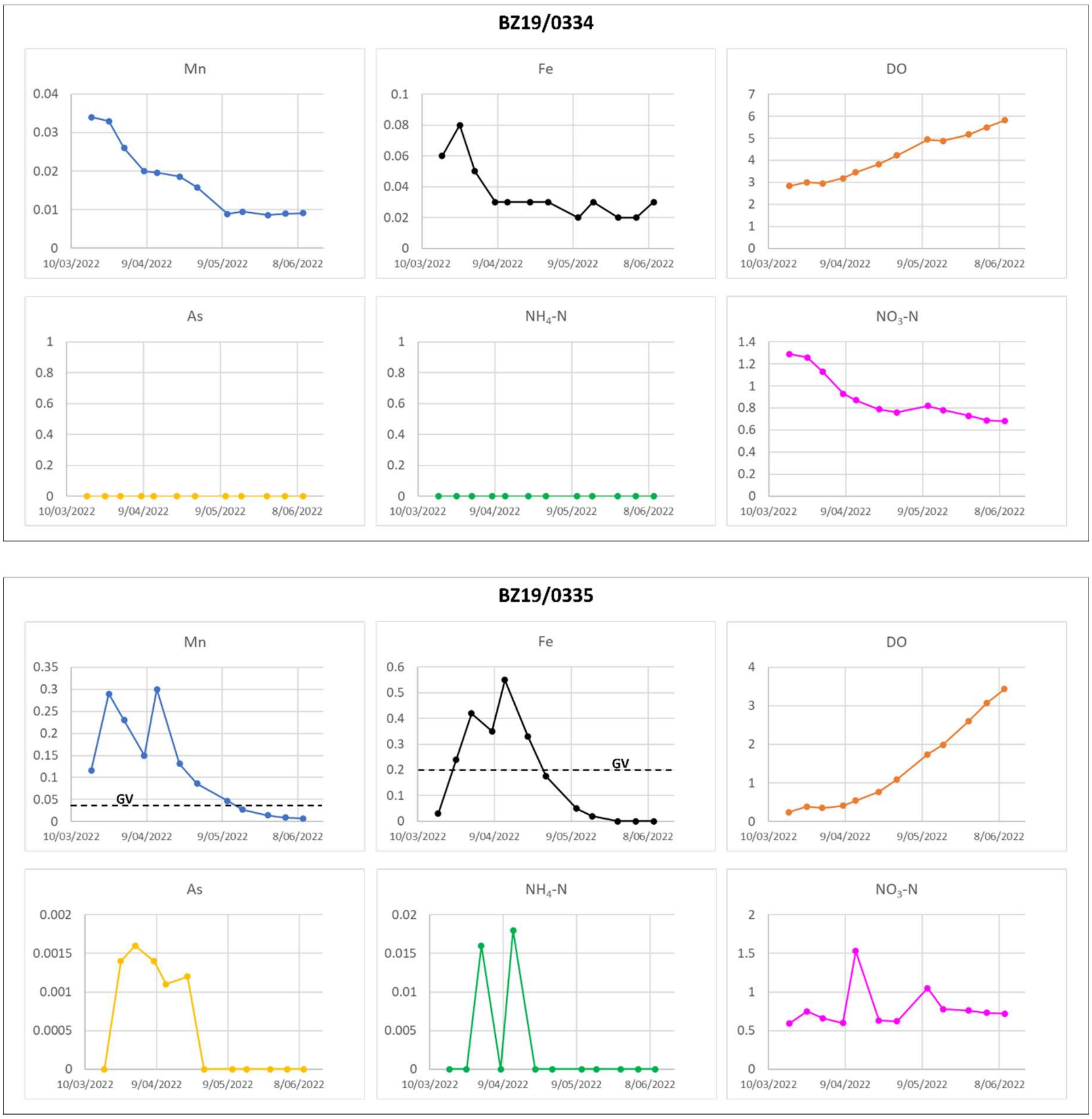
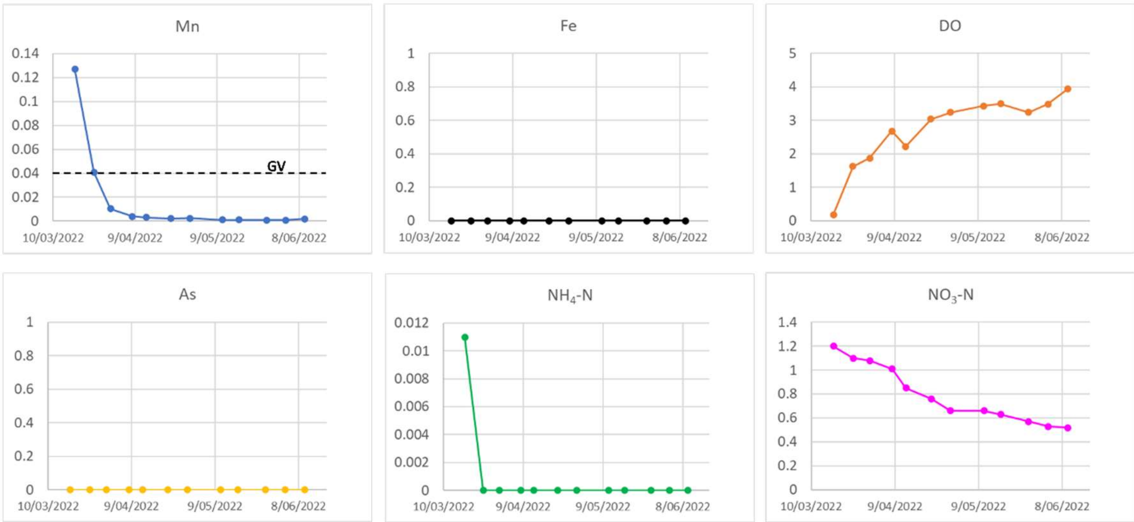
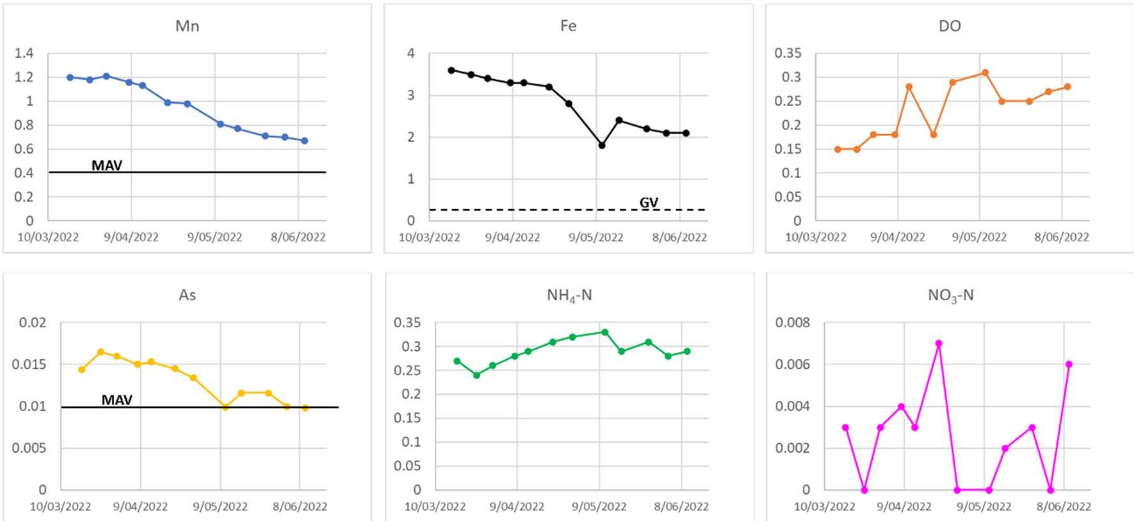


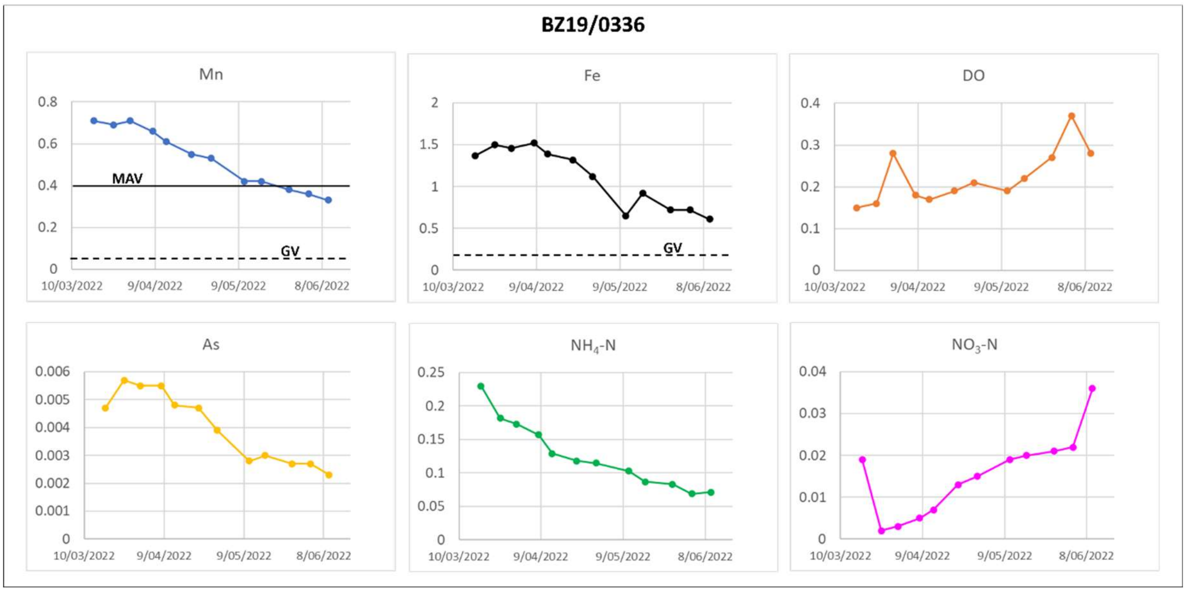
Figure 2: *Groundwater sampling results for upgradient monitoring wells. Units are in mg/L. Note that the vertical axis scale differs for each monitoring well. Mn: dissolved manganese, Fe: dissolved iron, DO: dissolved oxygen, As: dissolved arsenic, NH_4-N: ammonium, NO_3-N: nitrate nitrogen. GV: aesthetic-based guideline value (Drinking-water Standards for New Zealand, 2018).*

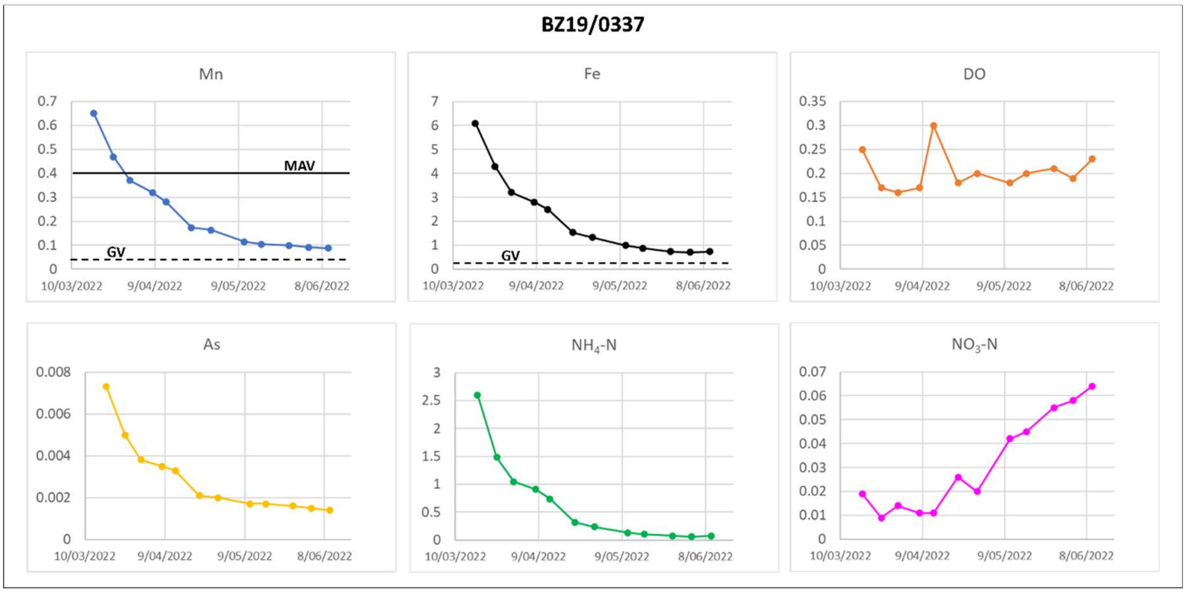
BZ19/0330



BZ19/0332




BZ19/0336
Mn
MAV
GV
Fe
GV
DO
As
NH4-N
NO3-N
10/03/2022
9/04/2022
9/05/2022
8/06/2022


BZ19/0337
Mn
MAV
GV
Fe
GV
DO
As
NH4-N
NO3-N
10/03/2022
9/04/2022
9/05/2022
8/06/2022

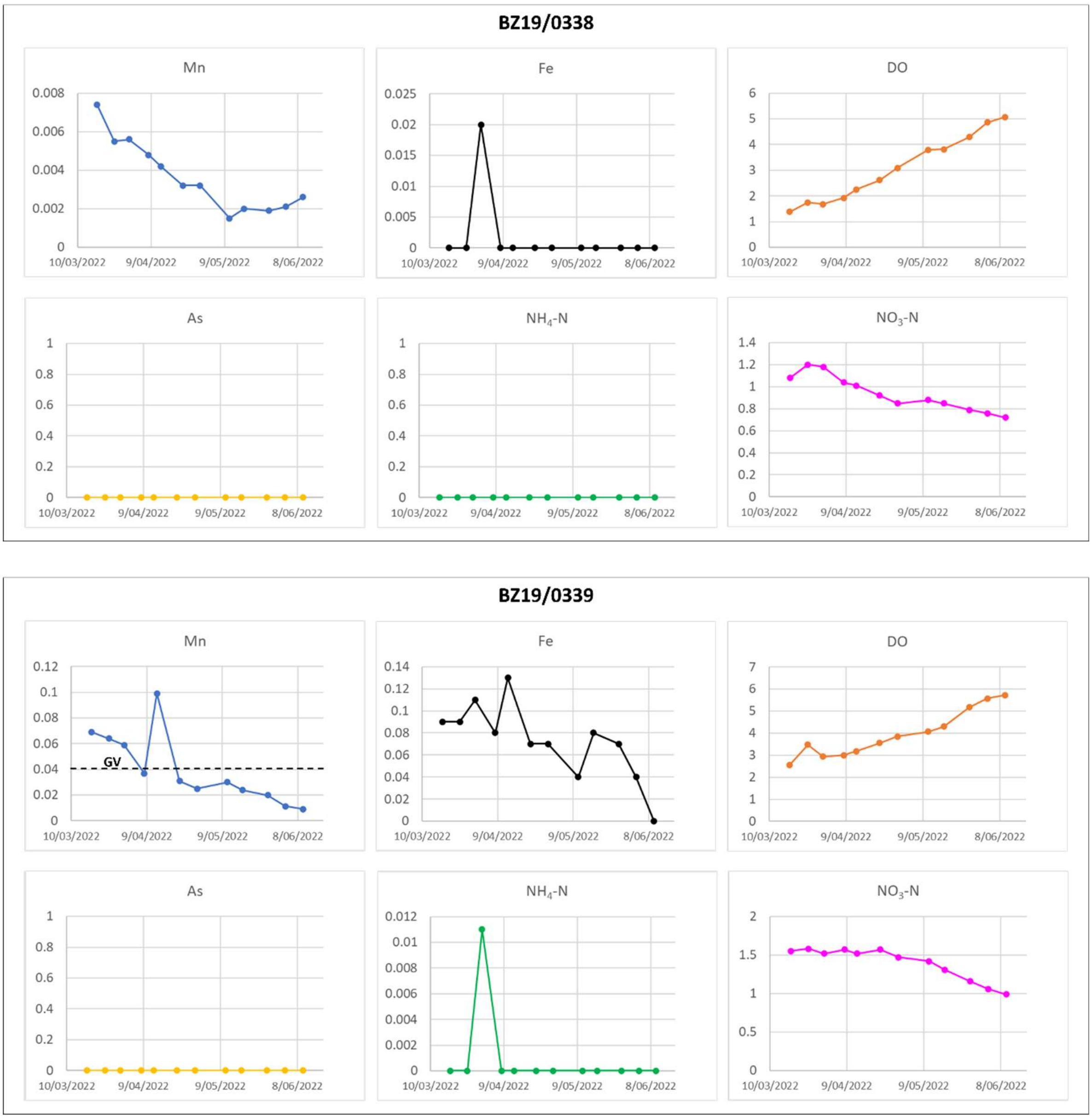


Figure 3: *Groundwater sampling results for downgradient monitoring wells. Units are in mg/L. Note that the vertical axis scale differs for each monitoring well. Mn: dissolved manganese, Fe: dissolved iron, DO: dissolved oxygen, As: dissolved arsenic, NH_4-N: ammonium, NO_3-N: nitrate nitrogen. GV: aesthetic-based guideline value, MAV: maximum acceptable value (Drinking-water Standards for New Zealand, 2018).*

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Appendix 2 – Peer review

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E/S/R Science for Communities He Pūtaiao, He Tāngata

1 August 2022

Review of Memo for Environment Canterbury:
Science Advice regarding elevated Mn in TDC Opihi water intake

Reviewed by Murray Close, Manager Groundwater, ESR

I have read through the memo describing issue of water discolouration caused by elevated levels of Mn in the Opihi water supply intake gallery, the prior and subsequent water quality sampling, and the likely causes of the elevated Mn levels.

I agree with the findings that are set out in the key points.

The following comments and suggestions are not in conflict with the key points but may add greater understanding to the events that took place and may provide some thoughts regarding guidance to prevent similar occurrences in the future.

We have noted similar rises in Mn concentration in shallow groundwater in response to increase of dissolved organic carbon (DOC) at one of our research sites. At our site in the Silverstream Reserve just north of Christchurch we introduced woodchips into the groundwater via a permeable reactive barrier (PRB) to reduce high nitrate concentrations in the shallow groundwater. The PRB was extremely effective in reducing nitrate levels but the reduced groundwater also mobilised metals such as Fe, Mn and As. This was expected and the concentrations of these metals were monitored over time with arrays of monitoring wells to determine the extent, in time and space, of these increases. The increases related to an input of labile (reactive) DOC which lasted < 6 months and the increases in Mn concentrations were restricted to within 60 m of the PRB. This is reported in much more detail by Burbery et al. (2022). The extent of mobilisation and the distance of travel will depend on the amount and type of DOC released and the hydrogeologic situation. For the Opihi situation the type of DOC released from silage is likely to be extremely reactive and result in a highly reduced leachate.

There is no information given in the memo about the likely travel time between the silage storage area and the gallery. This could be useful for interpretation of the changes in groundwater quality that have been observed and it could be used to provide a warning in the future. It should be noted that the travel times will be influenced by the pumping regime for the gallery.

There is a footnote on p4 that notes that there was more than 20 mm of rainfall in mid- and late March 2022. This was thought to relate to dilution of Mn concentration in some monitoring wells by rainfall recharge. On looking further at the rainfall record from Kakahu Bush (from the ECan website) I note that in November and December 2021, there was 110 mm and 144 mm rainfall, respectively. This was followed in February by a further 162 mm. I suspect that the heavy rainfall in November and December may have initiated the recharge of leachate from the silage storage area into the groundwater. It may be worthwhile to carry out some simple water balance calculations to confirm this and get better understanding of the factors that may have initiated this situation.

It would be useful to document the history of the silage storage area at the site. This could be compared with estimates of recharge while silage is present to give an indication of whether leachate generation may have happened previously.

Occurrence of high recharge while silage is present could be used as a warning in the future for use of the gallery.

There is some variability observed in the rate of improvement in water quality in wells BZ19/0330 and BZ19/0332. The improvement in water quality is much quicker in well 330 compared to well 332. Figure 1 suggests that well 330 may be located on an old paleochannel where groundwater movement may be more rapid (presence of open framework gravels), with more rapid flushing by higher quality groundwater.

Reference

Burbery, L., Abraham, P., Sutton R., Close, M. 2022. Evaluation of pollution swapping phenomena from a woodchip denitrification wall targetting removal of nitrate in a shallow gravel aquifer. Science of the Total Environment 820: 153194. http://dx.doi.org/10.1016/j.scitotenv.2022.153194