Metals in rural streams

A synoptic survey to support further development of the FWMT

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Executive summary

This report has been commissioned by Healthy Waters (Auckland Council) as part of ongoing reviews and continuous improvement in the innovative Freshwater Management Tool (FWMT) programme. Information and recommendations contained here is purposely for advancing the FWMT as a key decision-making and reporting tool for water quality across the Auckland region.

To support the ongoing development and continuous improvement of the FWMT, AC saw a need for further data on metals in streams draining catchments with different rural land uses.

A synoptic survey was therefore performed in March 2022 to collect stream water quality data from different rural land uses across the Auckland Region. The main purposes of this survey were to identify possible differences between streams from different rural land uses and with modelled FWMT baseline results and provide recommendations for improved simulation by FWMT.

Streams for which the contributing catchment is mainly composed of forest, pasture or horticulture land use and which provides a safe access for sampling were identified using satellite images and Hydrologic Response Unit (HRU) layer and associated land use composition provided by AC from FWMT v1.0. Thirty-two sampling sites were initially identified, including 7 AC State of the Environment (SOE) stations for which no, or only few, metal data were available over the time period 1/1/2012 to 31/12/2016 used for hydrological and water quality calibration of the FWMT. Twenty-five sites were sampled by NIWA and analysed for ultra-trace metals while 3 were sampled by AC and analysed for trace metals as part of the monthly SOE monitoring. Four sites were not sampled as no flow was observed during the sampling mission.

Field copper (Cu) concentrations of the surveyed sites were relatively similar across all main rural land use categories. Median field Cu concentrations varied from 0.3 to 0.8 and 0.62 to 0.82 µg/L for DCu and TCu, respectively. Some extreme TCu values were reported for the forest (9.4 µg/L) and horticulture land uses (1.28 µg/L) which could be related to forest management practices (e.g., disease control) and possible exports from urban areas present in the catchment, respectively. Model copper results for the same sites during baseflow were about 10 times lower than the synoptic survey data (median of 0.07 µg/L and 0.05 µg/L for TCu and DCu respectively versus median of 0.62 µg/L and 0.50 µg/L for TCu and DCu respectively). The horticulture and mixed land use categories exhibited higher modelled concentrations (median of 0.10 and 0.15 µg/L TCu, respectively) than the forest and pasture categories modelled concentrations (median of 0.06 and 0.07 µg/L TCu, respectively). Such a difference amongst land uses was not identified from the field data.

Field zinc (Zn) concentrations of the surveyed sites were relatively similar across all main land use categories. Median field Zn concentrations varied from 0.6 to 1 and 0.53 to 1.44 µg/L for DZn and TZn, respectively. While the forest land use exhibited the lowest median TZn, it also exhibited the highest reported concentration (5.2 µg/L in Riverhead) which is consistent with previously reported high Zn concentration of another Riverhead Forest stream (SOE site Riverhead@Ararimu Valley Road) which may be specific to this forest, based on lower concentrations in streams draining other forested areas. Overall, modelled Zn concentrations for the synoptic survey sites were relatively consistent with the field data collected in March 2022. The main difference between modelled and field data was the greater variability modelled for the horticulture and mixed rural land uses compared to other the land use categories (as also observed for copper), while such a difference was not identified from the field data.

The water quality data collected in March 2022 and comparison to model results highlighted various influencing factors that could be of importance when selecting sites for model calibration purposes and water quality model development. These are:

- Rural sites with limited urban contributing areas (e.g.,<3%) should be targeted for rural land use model calibration purposes as greater percentages (e.g., 11% for one of the horticulture sites in this survey) could largely influence the catchment metal export behaviour and be responsible for greater metal exports.
- Forest management (e.g., pest/disease control using copper-based products) could be an important factor resulting in higher metal variability for this type of land use which should be accounted for by the modelling tool itself and/or when selecting representative sites for model calibration.
- The representativeness of each land use category data set should be increased by collecting data from multiple sites presenting a high percentage of either forest, horticulture or pasture land use across the Auckland Region. The use of only one or two sites for each land use category could introduce a bias and reduce the ability of the model to capture the variability and/or accuracy of the metal exports from each rural land use type.

1 Introduction

Auckland Council (AC) has developed the Freshwater Management Tool (FWMT), a process-based water quality accounting tool for the Auckland Region (Healthy Waters, 2020). This model simulates the generation, transport and fate of contaminants from land into freshwater environments based on factors such as climate/meteorology, land cover and land use, soils, slope, consented water takes and discharges. To support the continuous development of this tool, AC saw a need for further data on metals in streams draining catchments with different rural land uses.

The aim of the present work was therefore to :

- Undertake a synoptic survey of metal concentrations for different rural land uses
- Assemble and analyse data from the synoptic survey for notable differences with modelled FWMT baseline results
- Provide commentary about latter results, choice of calibration/validation locations for rural land types, make inferences on the consequences of calibration station choices and recommend improvements (if any) on targeted monitoring for better simulation and confidence in simulation of metal concentration, by FWMT (e.g., for Stage 2 development).

2 Methodology

2.1 Synoptic survey

Water quality stations with metal data used for calibration and validation of FWMT for rural catchments comprised 3 sites identified as mainly “forest” land use, 9 as “pasture” and 1 as “horticulture”. Three of these sites were used for calibration purposes while the others were used for validation purposes (Healthy Waters, 2020). The synoptic survey was designed to collect additional streams water quality data (total and dissolved copper and zinc) in these three categories of rural land uses.

Existing layers of streams and Hydrological Response Units (HRU) with associated land uses composition (ha) were provided by Auckland Council Healthy Waters. Both layers, along with satellite photography, were used to identify streams for which the contributing catchment was mainly composed of forest, pasture or horticulture land use. Land use composition, aspects (small, large, vegetated etc) and access to these streams was then checked using google maps and street view to rule out those with expected low or stagnant flow or improper or unsafe access.

This resulted in a list of 32 sites (Table 2-1) including 7 AC State of the Environment (SOE) stations for which no, or only few, metal data were available over the time period 1/1/2012 to 31/12/2016 used for hydrological and water quality calibration of the FWMT. During the field survey four sites from this list were identified as not adequate for sampling as no flow was observed and were therefore not sampled. The selected sites’ contributing catchment were on average 89% composed of a mixture of forest, pasture and horticulture land use – that is, there was minimal land use in the urban, open space or barren categories. Detailed catchment land use and main land use category attributed to each site are provided in Table 2-1 and Figure 2-1. The SOE sites were either sampled by NIWA, AC (as part of the monthly SOE monitoring) or both (identified by “NIWA”, “AC” and “NIWA-AC”, respectively, in Table 2-1). The 3 sites sampled both by NIWA and AC were sampled at the same time by both organisations in order to compare the effect of the different sampling and analysis methods used.

Table 2-1: List of sites identified for the synoptic survey.

Site Coordinates		Site ID		Land use				Percent of area of entire contributing catchment (%) (5)							
NZGD_POINT_X	NZGD_POINT_Y	NIWA Site ID	SOE ID (if applicable)	Main Land use Cat. (1)	Catchment main contributing land uses (2)	AC land use category (3)	Collection and analysis (4)	Developed	Forest	Horticulture	Mine Barren	Open Space	Pasture	other	Fores+Pasture+Horticulture
1741579.07	5903993.77	For_1		For	For		NIWA	0.7	98.2	0.0	0.0	0.0	0.0	1.1	98.3
1738815.45	5903582.79	For_2		For	For		NIWA	3.2	88.8	0.1	0.0	1.9	5.7	0.3	94.6
1777985.18	5911690.76	For_3		For	For		NIWA	1.0	67.7	0.3	0.1	4.8	25.5	0.7	93.5
1740635.83	5931420.50	For_4		For	For		NIWA	0.3	88.3	0.0	0.0	6.5	4.3	0.7	92.6
1738930.49	5937423.44	For_5		For	For		NIWA	0.2	57.4	0.1	0.0	41.7	0.0	0.5	57.6
1786700.00	5892817.00	For_6	Wairoa Trib-8568	For	For	Past	NIWA-AC	0.1	0.7	0.0	0.0	0.0	99.1	0.0	99.9
1799807.31	5904347.13	For_7		For	For/Past		NIWA	0.6	53.5	0.4	0.0	2.4	42.9	0.1	96.8
1744069.82	5976550.09	For_8		For	For		NIWA	2.5	87.4	0.4	0.0	8.4	0.3	0.9	88.2
1764248.49	5877089.06	Hort_2		Hort	Hort		NIWA	2.2	4.1	35.7	0.0	16.2	41.6	0.2	81.3
1738272.17	5927708.74	Hort_4		Hort	Hort		NIWA	2.4	1.0	31.8	0.0	8.0	56.4	0.4	89.2
1739593.80	5928720.06	Hort_6		Hort	Hort		NIWA	3.5	8.3	6.1	0.1	12.1	69.4	0.7	83.8
1744578.55	5913420.28	Hort_7		Hort	Hort		NIWA	11.0	33.7	11.7	0.0	12.8	30.5	0.3	75.9
1744745.52	5914423.73	Hort_8	Oratia-7955	Mix	For/Past/Hort	Hort	NIWA	9.7	45.7	12.6	0.0	8.5	23.0	0.4	81.4
1763471.43	5882142.03	Hort_9		Hort	Hort/Past		NIWA	1.9	0.9	64.5	0.0	3.8	28.7	0.3	94.0
1763596.08	5884610.70	Hort_10	Whangamaire-438100	Mix	Past/Hort	Hort	NIWA-AC	3.4	1.5	36.4	0.0	9.7	48.6	0.4	86.5
1739312.19	5928776.58	Hort_12	Kumeu-45313	Mix	Past/Hort		NIWA-AC	3.5	8.3	6.1	0.1	12.1	69.4	0.7	83.8
1788065.74	5888763.02	Past_1		Past	Past		NIWA	1.5	10.6	0.8	0.0	10.4	76.5	0.1	88.0
1787510.94	5889903.24	Past_2		Past	Past		NIWA	1.5	0.1	2.2	0.0	1.0	94.9	0.4	97.2
1798178.22	5905126.75	Past_3		Past	Past		NIWA	0.6	1.9	0.2	0.0	1.1	96.2	0.0	98.3
1766411.41	5887532.96	Past_4		Past	Past		NIWA	2.6	1.0	15.5	0.0	10.7	69.7	0.5	86.2
1766051.97	5884961.89	Past_5		Past	Past		NIWA	0.7	0.1	15.3	0.0	9.0	74.7	0.2	90.1
1789370.25	5908598.30	Past_6		Past	Past		NIWA	0.1	0.0	0.0	0.0	0.0	99.9	0.0	99.9
1737168.33	5961356.41	Past_8		Past	Past		NIWA	1.7	11.9	2.7	0.0	8.7	74.5	0.4	89.1
1740613.27	5962132.12	Past_9		Past	Past		NIWA	1.8	12.5	1.3	0.0	0.7	83.4	0.3	97.2
1735286.61	5926171.26	Past_10		Past	Past		NIWA	1.3	3.7	2.5	0.0	9.9	82.3	0.3	88.5
1747747.50	5965036.81		Mahurangi Forestry-6811	For	For		AC	0.0	87.8	0.0	0.0	8.9	2.8	0.5	90.6
1735620.23	5916387.74		Cascades Stream-44603	For	For	For	AC	0.9	96.0	0.0	0.0	0.0	0.0	3.1	96.0
1775184.32	5881702.74		Ngakoroa-43829	Hort	Past/Hort/OS	Hort	AC	2.0	3.6	24.7	0.0	13.9	54.5	1.3	82.9
1766768.67	5880761.44	Hort_1		Hort	Hort		Discarded								
1756348.64	5976999.99	Hort_3		Hort	Hort		Discarded								
1736275.62	5929709.17	Hort_5		Hort	Hort		Discarded								
1738885.09	5968716.29	Past_7		Past	Past		Discarded								

(1) Land use category based on main land use of the whole contributing subcatchement. For: Forest, Hort: Horticulture, Past: Pasture, Mix: comprising significant contribution from at least two types of land uses.
(2) Catchment main contribution land uses based on main land use of the whole contributing subcatchement (data from FWMT_HRUComposition_Ha shape file provided by AC*) and/or aerial image. For: Forest, Hort: Horticulture, Past: Pasture, OS: Open space. Aerial images sometimes reflected different land use from HRU composition shape file and this was accounted for in the attributed land use category.
(3)AC land use category for SOE stations used for water quality calibration for the FWMT (Table 4-15 FWMT Baseline Configuration & Performance)
(4) NIWA: Sampled by NIWA and sent for ultra trace level dissolved and total Cu and Zn analysis, AC: sampled by AC and analysed in March 2022 as part of the monthly SOE monitoring (trace analysis), NIWA-AC: sampled both by NIWA and AC for sampling/analysis methods comparison, Discarded: no moving water so samples were discarded
(5) calculated using FWMT_HRUComposition_Ha shape file provided by AC*
* Land cover information generated for FWMT v1.0 HRU raster (e.g., indicative of 2013-2017 baseline land cover).

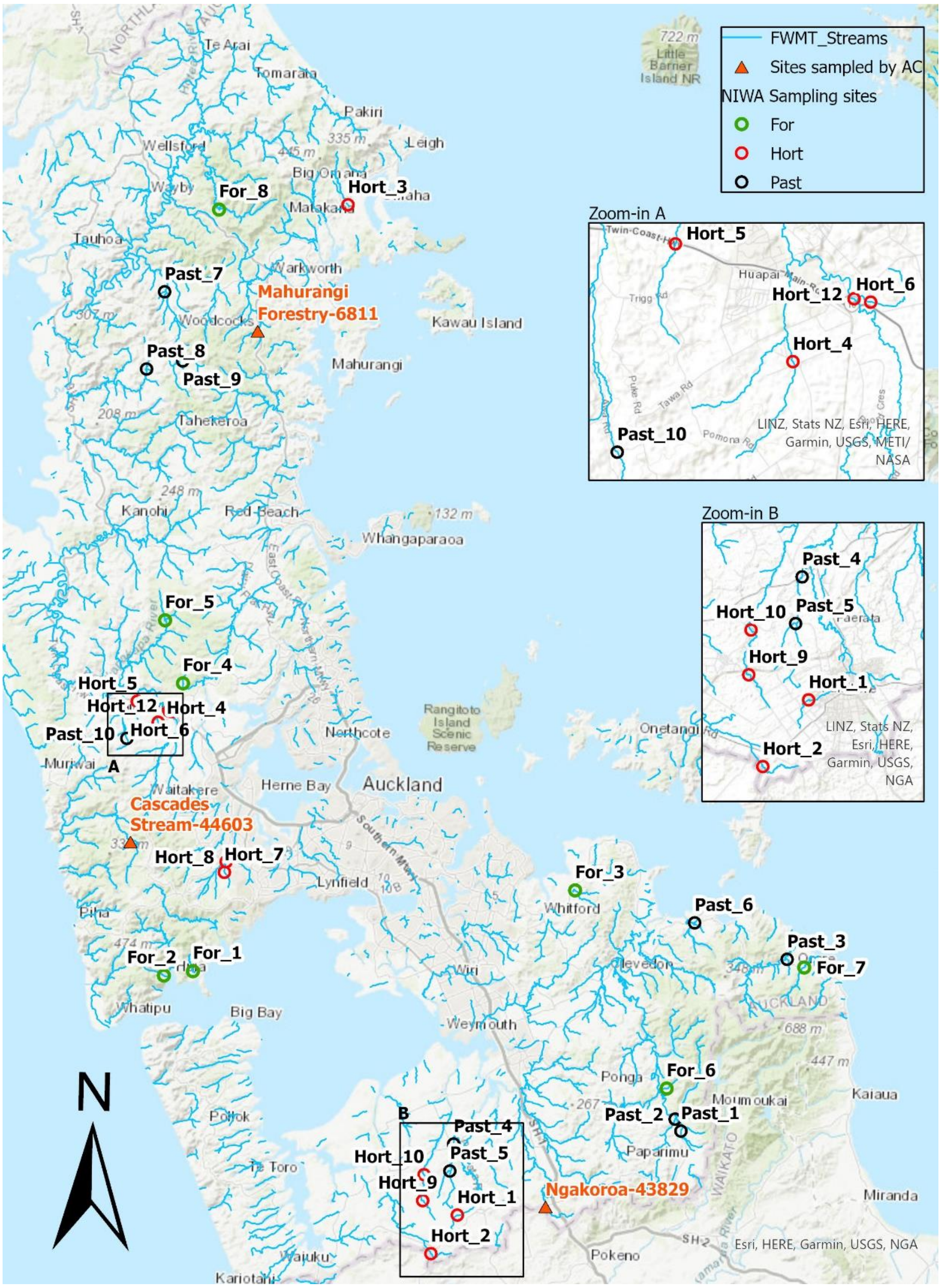

Figure 2-1: Location of synoptic survey sites. "NIWA Site ID" are displayed for sites sampled by NIWA and/or AC and SOE IDs are displayed for sites sampled only by AC, Table 2-1.

The synoptic survey was performed in March 2022. Samples collected by NIWA were collected following a "clean hand-dirty hand" sampling methodology to minimise contamination of the samples. Similarly to method 1669 (USEPA, 1996) upon arrival at the sampling site, one member of the two-person sampling team was designated as "dirty hands"; the second member was designated as "clean hands." All operations involving contact with the sample bottle and transfer of the sample to the sample bottle were handled by the individual designated as "clean hands." "Dirty hands" was responsible for handling field equipment and for all other activities that do not involve direct contact with the sample.

Samples collected by NIWA were filtered (for dissolved metal analysis) and acidified (for dissolved and total metal analysis) on site and kept on ice before being stored at 4°C at NIWA's laboratory prior to being sent to Hill Laboratories. Ultra trace metal analyses were performed as per Table 2-2. Samples collected by AC were sent to Hill Laboratory for filtering and analysis. For these samples trace metal analyses were performed as per Table 2-2. Standard uncertainty of laboratory analytical methods are 0.17 and 0.18 µg/L for DCu and TCu respectively and 0.33 and 0.37 µg/L for DZn and TZn, respectively.

Table 2-2: Hill Laboratories analytical methods used for analysis of samples collected by NIWA and by AC.

Collected by	Parameter	Analysis	Methods	Detection Limit
NIWA	Dissolved copper (DCu)	Ultra trace	ICP-MS, ultratrace level. APHA 3125 B 23rd ed. 2017.	0.0002 mg/L
	Total copper (TCu)	Ultra trace	Nitric acid digestion APHA 3030 E (modified) 23rd ed. 2017, ICP-MS, ultratrace level. APHA 3125 B 23rd ed. 2017	0.00021 mg/L
	Dissolved zinc (DZn)	Ultra trace	ICP-MS, ultratrace level. APHA 3125 B 23rd ed. 2017.	0.0005 mg/L
	Total Zinc (TZn)	Ultra trace	Nitric acid digestion APHA 3030 E (modified) 23rd ed. 2017, ICP-MS, ultratrace level. APHA 3125 B 23rd ed. 2017	0.00053 mg/L
AC	Dissolved copper	Trace	ICP-MS, trace level. APHA 3125 B 23rd ed. 2017.	0.0005 mg/L
	Total copper	Trace	Nitric acid digestion APHA 3030 E (modified) 23rd ed. 2017, ICP-MS, trace level. APHA 3125 B 23rd ed. 2017	0.00053 mg/L
	Dissolved zinc	Trace	ICP-MS, trace level. APHA 3125 B 23rd ed. 2017.	0.001 mg/L
	Total Zinc	Trace	Nitric acid digestion APHA 3030 E (modified) 23rd ed. 2017, ICP-MS, trace level. APHA 3125 B 23rd ed. 2017	0.0011 mg/L

2.2 Synoptic survey water quality data and model results analysis

The main contributing land uses of the surveyed sites' catchment were computed from the data provided by AC (FWMT_HRUComposition_Ha shape file) and/or aerial images. Aerial images sometimes reflected different land use from AC HRU composition shape file and this was accounted for in the attributed land uses. The resulting catchment main contributing land uses are presented in Table 2-1 (6^{th} column). Surveyed sites were then grouped in 4 land use categories based on the main land use of the whole contributing catchment, i.e. For: Forest, Hort: Horticulture, Past: Pasture, Mix: comprising significant contribution from at least two types of land uses (Table 2-1, 5^{th} column).

Synoptic survey metal concentrations were analysed to identify variability, extremes and differences amongst the four main land use categories. Extreme values and outliers are defined as:

$$extreme\ values > (75^{th} th\ percentile + 3\ \times interquartile\ range)$$

$$extreme\ values > outliers > (75^{th} th\ percentile + 1.5\ \times interquartile\ range)$$

They were then compared to copper and zinc model results generated for the same sites (excluding Mahurangi Forestry-6811 for which no model results were available). As the synoptic survey was performed during dry weather, only model results during baseflow conditions (when flow was lower or equal to the median flow over the modelling period) were used for the data analysis.

3 Results

3.1 Field data quality and selection for analysis

Amongst the 28 surveyed sites, one appeared to be saline (For_1) requiring an analytical method with higher DLs (1-1.1µg/L for D-TCu, 4-4.2µg/L for D-TZn). The results for that specific site were <DLs and therefore were discarded from the data analysis. The remaining 24 sites sampled by NIWA and analysed using ultra trace methods were all above the DLs except for 1 sample for TCu, 4 for DCu, 8 for TZn and 7 for DZn. The 3 sites sampled only by AC and analysed for trace metals were all below the DLs except for the copper analysis for 1 sample.

When analytical results of samples analysed for ultra trace metals were below DLs, the samples concentrations were replaced by the DLs for the purpose of data analysis. When analytical results of samples analysed for trace metals were below trace methods DLs (which are higher than ultra trace DLs), sample results were discarded to avoid overestimating metals for these sites. When both ultra trace and trace analyses were performed for a site ultra trace data was used for data analysis.

Ultra trace dissolved analyses were sometimes greater than that for the total fraction, but within analytical variation of the method (+/-0.15µg/L for DCu and +/-0.34µg/L for DZn).

The raw data from the laboratory for each individual site are provided in Appendix A.

Three sites were analysed both for ultra trace and trace dissolved and total copper and zinc representing a total of 12 trace and 12 ultra trace analyses (Table 3-1). When metals were detected by both analytical methods (3 occurrences over 12), trace and ultra trace concentrations were relatively similar (with a relative percent difference ranging from -5 to 13.3%) and within analytical variation of the methods. While the ultra trace method detected metals in 9 samples over 12, the trace method detected metals in only 3 samples over 12 suggesting that ultra trace method would be more adequate when analysis rural streams metal concentrations (especially for Zn which was never detected with the trace method, Table 3-1). No apparent metal contamination was detected between the samples collected by NIWA as per the clean hand-dirty hand method (followed by on-site filtering for dissolved metals) and the samples collected by AC.

Table 3-1: Trace and ultra trace Cu and Zn analyses for the 3 sites which were sampled both by NIWA and AC.

	TCu- ultra trace	TCu_Trace	DCu- ultra trace	DCu_Trace	TZn- ultra trace	TZn_Trace	DZn- ultra trace	DZn_Trace
Detection limit (µg/L)	0.21	0.53	0.2	0.5	0.53	1.1	0.5	1
Kumeu-45313	0.82	0.77	0.8	0.7	1.24	<1.1	1.1	<1
Wairoa Trib-8568	0.59	0.62	0.6	<0.5	<0.53	<1.1	0.6	<1
Whangamaire-438100	0.4	<0.53	0.4	<0.5	<0.53	<1.1	<0.5	<1

(green) metal detected by both analytical methods
(yellow) <DL

3.2 Results of synoptic stream survey

3.2.1 Copper

Field copper (Cu) concentrations of the surveyed sites (in March 2022) were relatively similar across all main land use categories (Figure 3-1). Median field Cu concentrations varied from 0.3 to 0.8 and 0.62 to 0.82 µg/L for DCu and TCu, respectively. Some extreme TCu values were reported for the forest (For_7: 9.4 µg/L) and horticulture land uses (Hort_7: 1.28 µg/L).

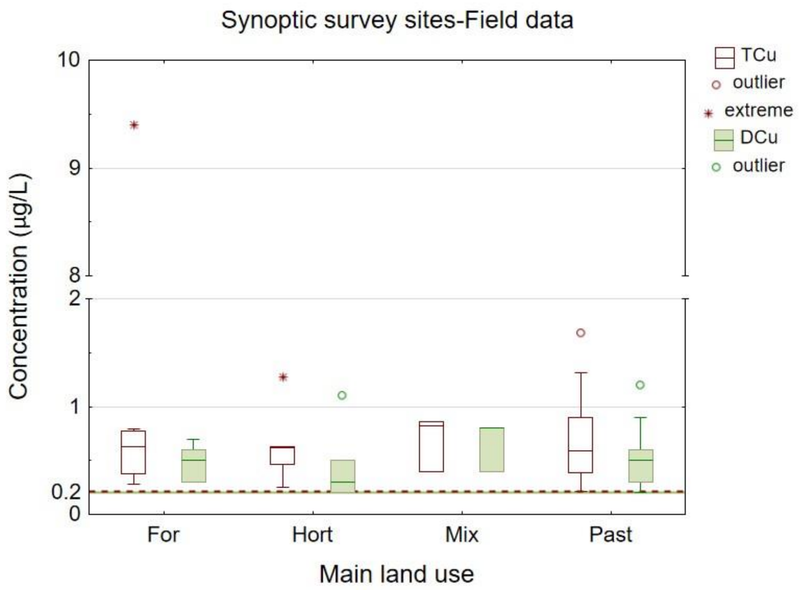

Figure 3-1: Field copper concentrations of surveyed sites with a contributing catchment comprising mainly forest (For), horticulture (Hort), pasture (Past) or a mixed (Mix) rural land use. A scale break between 2 and 8 µg/L has been implemented on the Y axis. The green line represents DCu detection limit =0.2 µg/L, the red dashed line represents TCu detection limit=0.21µg/L. Extreme values are defined as values >(75th percentile+3 x interquartile range) and outliers are defined as values >(75th percentile+1.5xinterquartile range) and <extreme values.

Although the closest area to Hort_7 is mainly horticulture and a bit of forest, this site's catchment presents the highest proportion of developed area amongst the horticulture land use category sites (11% of the catchment compared to 2-3.5 % for the other "horticulture" sites) . This might have impacted copper export within the catchment and could be responsible for the relatively higher TCu concentration, however other specific sources or practices in this catchment cannot be ruled out.

It is unclear why For_7 exhibited such high TCu concentrations compared to the other “Forest” sites and could be indicative of either specific geological conditions or Cu generating activities in the catchment. For_7’s catchment land use is mainly indigenous forest (Figure 3-2) and some pasture (~50 Ha) located close to the sampling site. While pasture is not generally known to be a copper releasing activity, the most common cause of copper export from forest would be copper fungicides spraying in case of vegetation diseases (Baillie et al., 2017). Satellite images over 2015-2021 suggest that some parts of the forest covered by Manuka and/or Kanuka may have suffered from a disease over the years and the vegetation was partly cut during the second half of 2021 (Figure 3-2 and Figure 3-3). Whether or not copper based fungicide has been applied is not known and therefore no assertion can be made regarding the source of Cu at this stage, but it suggests that management specific to each forest could be an important factor resulting in higher metal variability for this type of land use which is not currently accounted for by the FWMT.

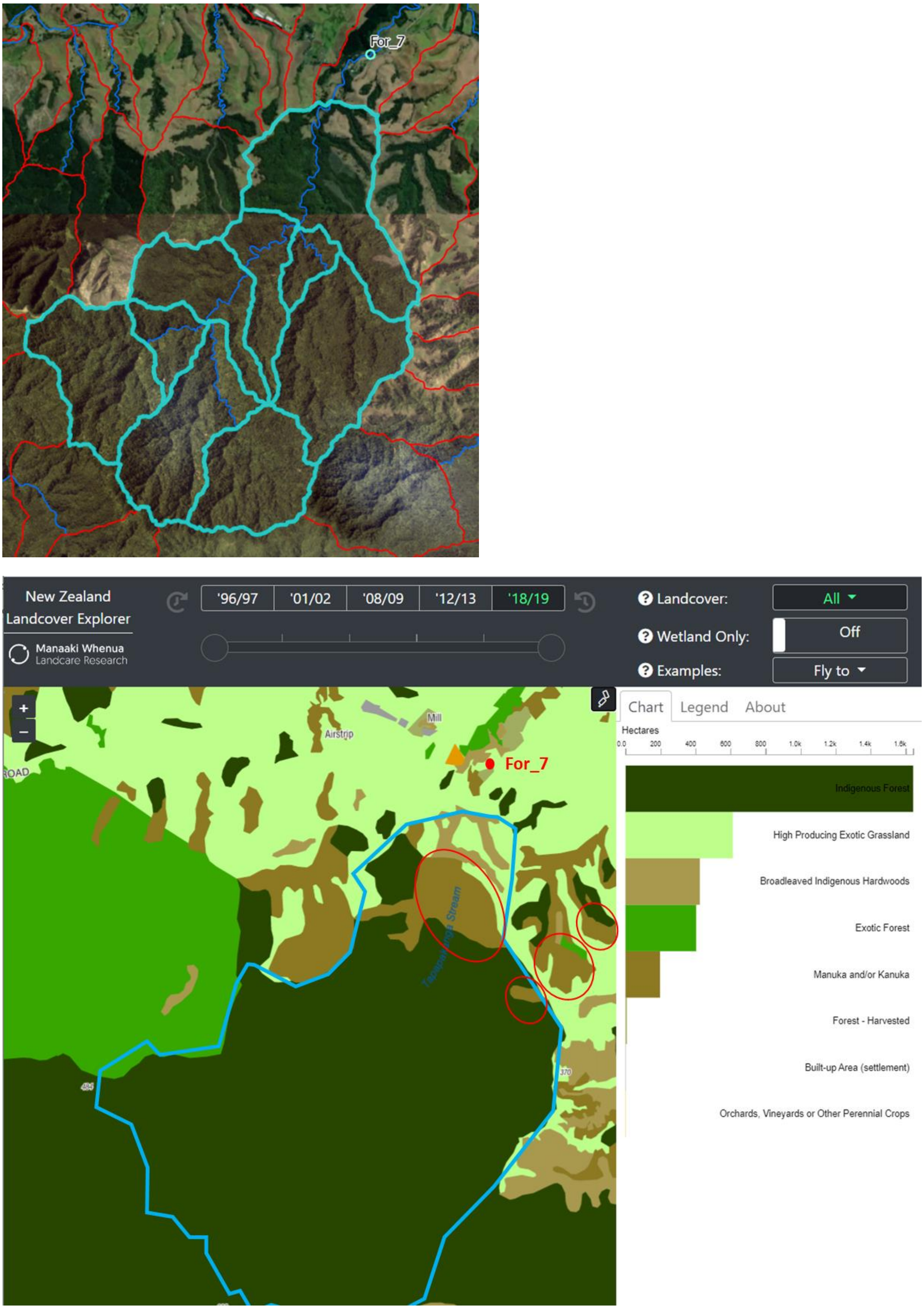

Figure 3-2: Hydrological response units upstream of For_7 (in light blue, top picture) and associated land cover (bottom picture, New Zealand Landcover Explorer/Landcare Research). Red circles refer to the same circles on Figure 3-3.

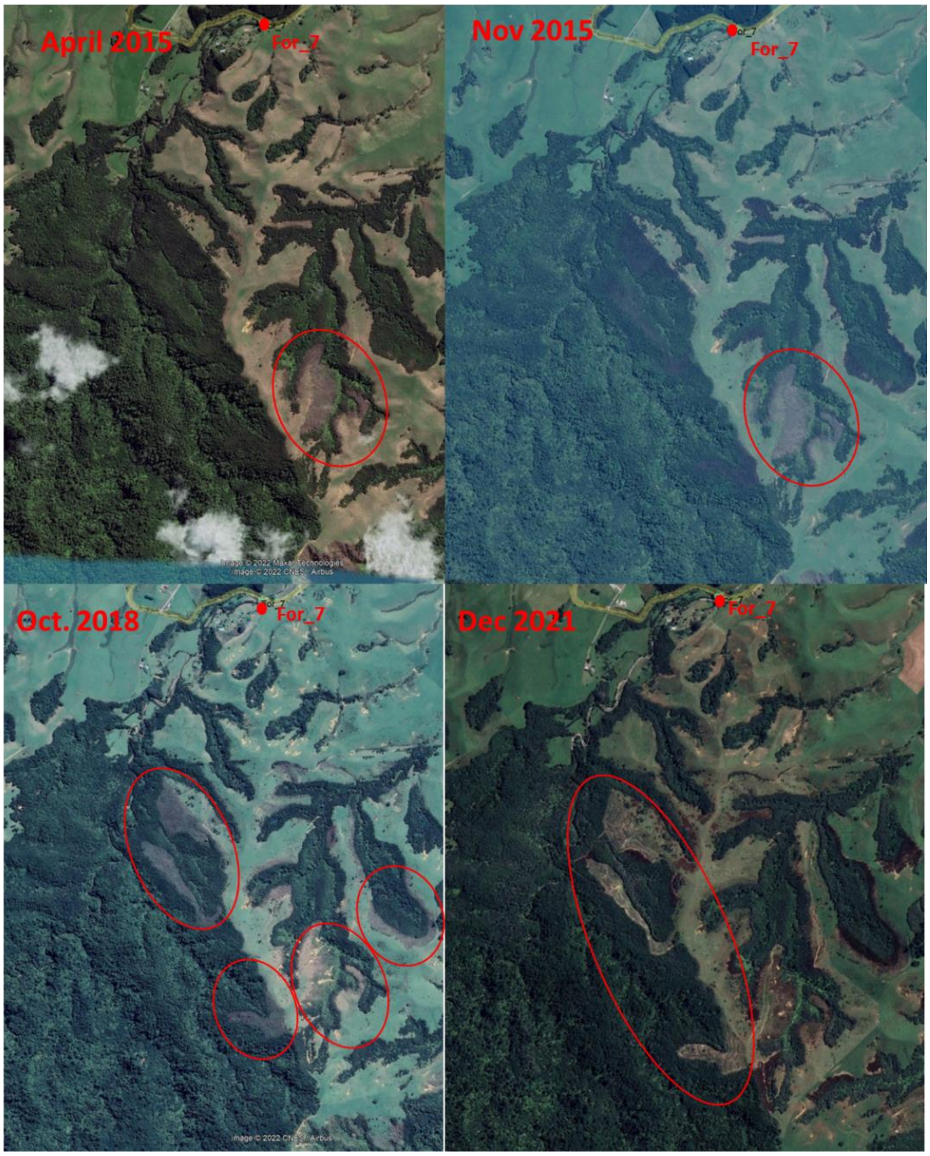

Figure 3-3: Satellite images of areas close to For_7 showing the presence of potential disease spreading to the vegetation over 2015-2021 (red circles) and vegetation removal in 2021 (red circle).

3.2.2 Zinc

Field zinc (Zn) concentrations of the surveyed sites were relatively similar across all main land use categories (Figure 3-4). Median field Zn concentrations varied from 0.6 to 1 and 0.53 to 1.44 µg/L for DZn and TZn, respectively. While the forest land use exhibited the lowest median TZn (mainly due to the relative high number of samples <DL; 57% of the "forest" samples compared to 20-33% for the other land uses categories) it also exhibited the highest reported concentration (5.2 µg/L TZn and 4.5 µg/L DZn for For_4).

The catchment of For_4 includes part of the exotic Riverhead Forest for which high stream Zn concentrations have been reported in the past decade at the SOE site Riverhead@Ararimu Valley Road / 45373 based on monthly monitoring. Reported concentrations ranged from 2 to 47 µg/L over 2010-2021 with a median of 7.6 µg/L. For_5 whose catchment also comprises part of the Riverhead Forest exhibited the second highest Zn concentration for the forest land use category. The present synoptic survey data are therefore consistent with previously reported high Zn concentration of

Riverhead stream for which the source has not yet been identified. These elevated Zn concentrations seem to be localised to the Riverhead Forest as 5 forest land use category sites investigated during the synoptic survey (including two other exotic forests) were below or just above (0.55 µg/L) the detection limit of 0.53 µg/L and 2 native "forest" sites analysed for trace metals were <1.1 µg/L (trace method DL). The Riverhead@Ararimu Valley Road / 45373 is one of the two sites with significant percentage of forest land cover used to calibrate the FWMT for metals. Given its relatively higher Zn concentration this site might not be representative enough of the Auckland Region "forest" land use for the purpose of model calibration.

Two extreme values were also observed for the pasture land use category (3.1 µg/L for Past_4 and 2.6 for Past_1) however the probable causes for these higher concentrations remains unclear. At least 70% of both sites' contributing catchment is pasture suggesting a dominant effect of this land use. A large farming site (including about 4 ha of sheds, silos and ponds) is located about 1.7 km upstream of Past_4 and could contribute to the elevated zinc concentration.

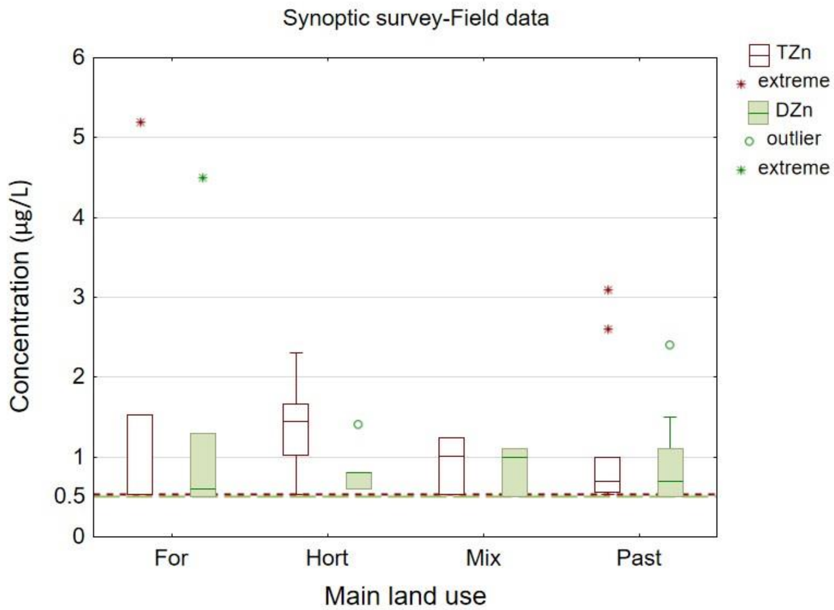

Figure 3-4: Field zinc concentrations of surveyed sites with a contributing catchment comprising mainly forest (For), horticulture (Hort), pasture (Past) or a mixed (Mix) rural land use. The green line represents the DZn detection limit =0.5 µg/L, the red dashed line represents TZn detection limit=0.53µg/L. Extreme values are defined as values >(75th percentile+3 x interquartile range) and outliers are defined as values > (75th percentile+1.5xinterquartile range) and <extreme values.

3.3 Comparison of field and modelled metals data

Model copper results during baseflow (median of 0.07 µg/L and 0.05 µg/L for TCu and DCu respectively) were about 10 times lower than the synoptic survey data (median of 0.62 µg/L and 0.50 µg/L for TCu and DCu respectively). While the copper concentrations were relatively consistent over the various land use categories for the field data (Figure 3-5), the horticulture and mixed land use categories exhibited higher modelled concentrations (median of 0.10 and 0.15 µg/L TCu, respectively) than the forest and pasture categories modelled concentrations (median of 0.06 and 0.07 µg/L TCu, respectively, Figure 3-5).

The field data interquartile ranges were relatively consistent over the different land use categories (0.3 to 0.51 µg/L Cu) while a stronger difference was observed amongst the land use categories modelled results with the horticulture and rural mixed land use categories exhibiting interquartile ranges 10 times higher than the forest and pasture land use categories (0.16-0.22 versus 0.01-0.02 µg/L Cu).

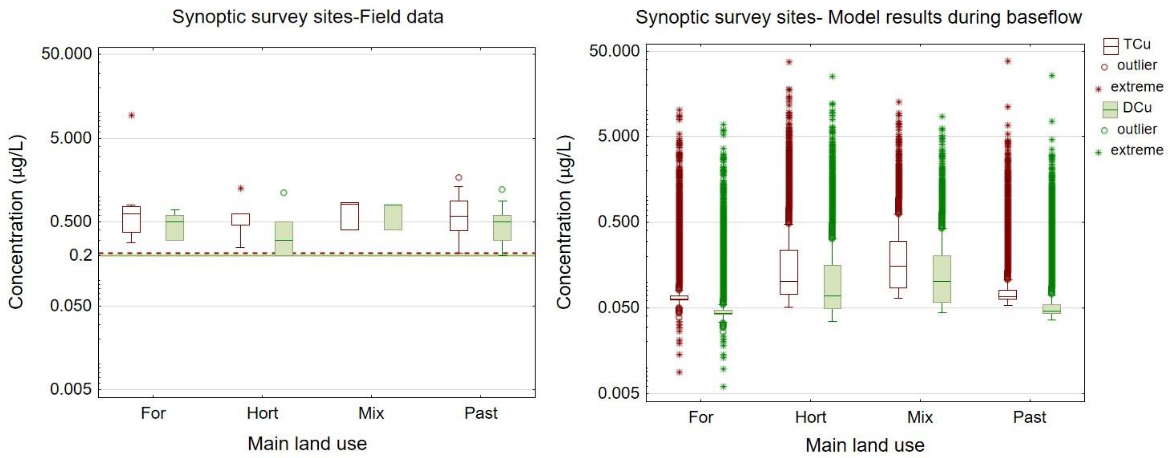

Figure 3-5: Field and modelled (during baseflow conditions) copper concentrations of surveyed sites with a contributing catchment comprising mainly forest (For), horticulture (Hort), pasture (Past) or a mixed (Mix) rural land use. Y axis is on a logarithmic scale. The green line represents the DCu detection limit =0.2 µg/L, the red dashed line represents TCu detection limit=0.21µg/L. Extreme values are defined as values >(75th percentile+3 x interquartile range) and outliers are defined as values > (75th percentile+1.5xinterquartile range) and <extreme values.

Model zinc results during baseflow (median of 1.04 µg/L and 0.71 µg/L for TZn and DZn respectively) were of the same order of magnitude as the synoptic survey data (median of 0.78 µg/L and 0.65 µg/L for TZn and DZn respectively). Zn concentrations were relatively consistent over the various land use categories for both the field and modelled data (Figure 3-5). Similarly to Cu, the field Zn data interquartile ranges were relatively consistent over the different land use categories (0.2 to 1 µg/L Zn) while a stronger difference was observed amongst the land use categories modelled results with the horticulture and rural mixed land use categories exhibiting higher interquartile ranges than the forest and pasture land use categories (0.59-1.47 versus 0.04-0.12 µg/L Zn).

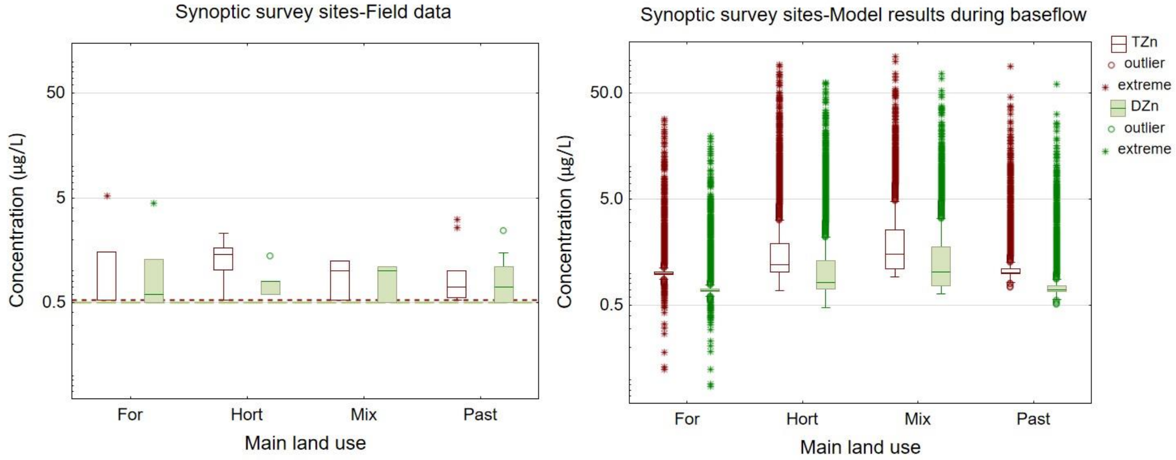

Figure 3-6: Field and modelled (during baseflow conditions) zinc concentrations of surveyed sites with a contributing catchment comprising mainly forest (For), horticulture (Hort), pasture (Past) or a mixed (Mix) rural land use. Y axis is on a logarithmic scale. The green line represents the DZn detection limit =0.5 µg/L, the red dashed line represents TZn detection limit=0.53µg/L. Extreme values are defined as values >(75th percentile+3 x interquartile range) and outliers are defined as values > (75th percentile+1.5xinterquartile range) and <extreme values.

Overall, Zn model results for the synoptic survey sites were relatively consistent with the field data collected in March 2022. The main difference was the greater variability modelled for the horticulture and mixed rural land uses compared to other the land use categories (as also observed for copper), while such a difference was not identified from the field data.

The inconsistencies between metals field data and modelled results reported above suggest that:

- the model might not have been able to capture the variability and intensity of copper exports from rural land use due to the relatively low number of reference sites comprising high percentages of forest, horticulture or pasture land use to calibrate the model (i.e., only 1 or 2 sites were available for each land use with metal data over 2012-2016)
- and/or the relatively low number of field data point collected during the synoptic survey for each land use category (N=3 to 9) compared to the number of modelled results (N=2739 to 8217) reduced the chances of capturing the full range of rural streams field metal concentrations.

4 Recommendations

The water quality data collected in March 2022 from various rural streams with catchments dominated by forest, pasture, horticulture or mixed rural land use highlighted various influencing factors that could be of importance during site selection for model calibration purposes and water quality model development. These are:

- Rural sites with limited urban contributing areas (e.g., <3%) should be targeted for rural land use model calibration purposes as greater percentages (e.g., 11% for Hort_7) could largely influence the catchment metal export behaviour and be responsible for greater metal exports.

- Forest management (e.g., pest/disease control using copper-based products) could be an important factor resulting in higher metal variability for this type of land use which should be accounted for by the modelling tool itself and/or when selecting representative sites for model calibration.
- The representativeness of each land use category data set should be increased by collecting data from multiple sites presenting a high percentage of either forest, horticulture or pasture land use across the Auckland Region. The use of only one or two sites for each land use category could introduce a bias and reduce the ability of the model to capture the variability or accuracy of the metal exports from each rural land use.

5 Acknowledgements

The authors would like to acknowledge Christian Hyde and Jessie Scarrott (NIWA) who collected the stream water samples for analysis. We would also like to acknowledge the support of Auckland Council RIMU staff in discussions regarding sites, in coordinating field work in March 2022 during the synoptic survey, and for subsequent sharing of data to be included in this report. It is to be noted that AC data were shared before the full QA/QC process could be performed.

6 References

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Appendix A Synoptic survey sites copper and zinc analyses

				Ultra trace analyses				Other analyses (for saline samples or trace method)			
sampling date	NIWA Site ID	SOE ID (if applicable)	Sampled by	TCu (µg/L)	Dcu (µg/L)	TZn (µg/L)	DZn (µg/L)	TCu (µg/L)	DCu (µg/L)	TZn (µg/L)	DZn (µg/L)
10/03/2022	For_1		NIWA					<1.1	<1	<4.2	<4
10/03/2022	For_2		NIWA	0.79	0.7	<0.53	<0.5				
10/03/2022	For_3		NIWA	0.28	0.3	0.55	0.6				
7/03/2022	For_4		NIWA	0.75	0.6	5.2	4.5				
7/03/2022	For_5		NIWA	0.36	0.3	1.53	1.3				
30/03/2022	For_6	Wairoa Trib-8568	NIWA-AC	0.59	0.6	<0.53	0.6	0.62	<0.5	<1.1	<1
10/03/2022	For_7		NIWA	9.4	0.3	<0.53	<0.5				
8/03/2022	For_8		NIWA	0.4	0.4	<0.53	<0.5				
30/03/2022	Hort_2		NIWA	0.62	0.5	1.02	0.6				
7/03/2022	Hort_4		NIWA	0.46	<0.2	1.44	0.8				
7/03/2022	Hort_6		NIWA	0.63	<0.2	2.3	0.6				
10/03/2022	Hort_7		NIWA	1.28	1.1	1.67	1.4				
10/03/2022	Hort_8	Oratia-7955	NIWA	0.86	0.8	1.01	1				
30/03/2022	Hort_9		NIWA	0.25	0.3	<0.53	0.8				
30/03/2022	Hort_10	Whangamaire-438100	NIWA-AC	0.4	0.4	<0.53	<0.5	<0.53	<0.5	<1.1	<1
7/03/2022	Hort_12	Kumeu-45313	NIWA-AC	0.82	0.8	1.24	1.1	0.77	0.7	<1.1	<1
30/03/2022	Past_1		NIWA	1.32	1.2	2.6	2.4				
30/03/2022	Past_2		NIWA	0.56	0.6	0.86	1.1				
10/03/2022	Past_3		NIWA	0.59	0.5	<0.53	<0.5				
30/03/2022	Past_4		NIWA	1.68	0.3	3.1	1.5				
30/03/2022	Past_5		NIWA	0.9	0.9	1	1.1				
10/03/2022	Past_6		NIWA	<0.21	<0.2	0.7	0.7				
8/03/2022	Past_8		NIWA	0.63	0.6	0.56	<0.5				
8/03/2022	Past_9		NIWA	0.39	0.4	<0.53	<0.5				
7/03/2022	Past_10		NIWA	0.31	<0.2	0.67	0.6				

				Ultra trace analyses				Other analyses (for saline samples or trace method)			
sampling date	NIWA Site ID	SOE ID (if applicable)	Sampled by	TCu (µg/L)	Dcu (µg/L)	TZn (µg/L)	DZn (µg/L)	TCu (µg/L)	DCu (µg/L)	TZn (µg/L)	DZn (µg/L)
7/03/2022		Cascades Stream-44603	AC					0.66	0.6	<1.1	<1
30/03/2022		Ngakoroa-43829	AC					<0.53	<0.5	<1.1	<1
8/03/2022		Mahurangi Forestry-6811	AC					<0.53	<0.5	<1.1	<1