NIWA
Taihoro Nukurangi

Heavy metals state and trends in New Zealand rivers

Analyses of national data ending in 2022

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Executive summary

The Ministry for the Environment and Stats NZ/Tatauranga Aotearoa are required to report on the state of the environment using a pressure-state-impact framework, by the Environmental Reporting Act 2015. State of the environment reports and national indicators are produced by the joint Environmental Reporting Programme.

This report describes the update of the national indicator 'River water quality: Heavy metals' using the latest data available for Aotearoa New Zealand. The heavy metals indicator includes two metals that are key indicators of stormwater from urban areas: copper (dissolved) and zinc (dissolved). This report assesses the current state of these two indicators and trends over time at each site. This report uses data that have been collected by city councils, regional councils and unitary authorities across New Zealand.

This indicator has previously been reported on twice, the first time in 2016 (Gadd 2016) and the second time in 2019 (Gadd et al. 2019). Those assessments focussed on urban streams only (those streams/rivers with more than 15% urban land cover in the upstream catchment as defined by Snelder and Biggs (2002)), whereas in this assessment of state and trends, all sites with adequate monitoring data were included, regardless of upstream catchment land cover. Data were available from six regions in New Zealand (Auckland, Waikato, Bay of Plenty, Wellington, Canterbury and Otago) compared to only three in previous assessments (Auckland, Wellington and Christchurch City).

State: methods and findings

In the state assessment we used a five-year period (January 2017 to December 2022), consistent with use of a five-year period in national river water quality state assessments which did not include metals. This differs from the previous state assessments of dissolved copper and zinc that both used three-year periods (January 2013 to December 2015 and January 2015 to December 2017) to maximise the number of sites included. We also excluded data where this was identified by Councils as low quality.

We applied filtering rules based on minimum data requirements to provide an accurate and robust assessment of state for this indicator. The rule adopted for the state assessment was to include sites if there were 80% of observations within the time period. This was a change from the 90% threshold used previously and was relaxed due to the omission of low quality data which reduced the number of observations at some sites. We also assessed the state for sites that did not meet the minimum data requirements to provide an indication of state at a larger number of sites and across a greater geographic area. However, as there was greater uncertainty in the calculated state statistics for those sites, they were not included in the comparisons to water quality guideline values or when assessing relationships to land cover.

Only sites in Auckland, Wellington, Canterbury and Otago regions met the minimum data requirements, with 100 sites in total suitable for each metal. There were an additional 59 and 73 sites where dissolved copper and dissolved zinc were measured during the same period but where the data did not meet the minimum data requirements, including sites in Waikato and Bay of Plenty regions. There were no obvious differences in the metal concentrations between regions. Across New Zealand, higher metal concentrations were associated with higher proportions of urban land cover and impervious surface area in the catchment.

We compared dissolved copper and dissolved zinc concentrations to ANZECC/ARMCANZ (2000) default guideline values and to draft updated default guideline values that differ depending on dissolved organic carbon, water hardness and pH in the water (Anon 2022, Anon 2023). Sites with urban land cover upstream were associated with higher percentages of guideline value exceedance, regardless of the guidelines used (ANZECC/ARMCANZ or draft updates).

Trends: methods and findings

The methods used to assess the trends in dissolved copper and dissolved zinc were largely consistent with those used in Gadd et al. (2019), except for at sites where detection limits changed over time. In this assessment we used a hi-censor function – all observations that are less than the highest censored value (including those that are measured) are treated as censored values based on that highest censored value. This method is to ensure that changes in detection limits over time do not cause a trend in the data. A ten-year period was used to assess trends, consistent with the previous assessment. The minimum data requirements for trend assessment were to require observations in at least 80% of the months (or quarters) within the trend period, and that those observations were distributed across at least 80% of the years (i.e., there must be data for at least 8 years).

Although 71 sites met these minimum data requirements for trend assessment, trends could only be quantified at 50 and 65 sites for dissolved copper and dissolved zinc respectively, due to high proportions of censored data (particularly for copper). These sites were located in the Auckland, Wellington and Canterbury (Christchurch City) regions only.

There were degrading trends for dissolved copper at more than half of the sites (28 out of 50), whereas there were improving trends for dissolved zinc at more than half of the sites (36 out of 50). The overall degrading trends in dissolved copper nationally are largely because of degrading trends at all sites in the Auckland region (22 sites), compared to 5 out of 21 sites in Canterbury and 1 out of 7 sites in Wellington. For dissolved zinc, a slightly greater proportion of sites showed degrading trends in Canterbury (35%, 14 out of 40 sites) compared to the Auckland (16%, 3 out of 19) and Wellington regions (0%, none of the 6 sites).

1 Introduction

The Ministry for the Environment and Stats NZ/Tatauranga Aotearoa are required to report on the state of the environment using a pressure-state-impact framework, by the Environmental Reporting Act 2015. State of the environment reports and national indicators are produced by the joint Environmental Reporting Programme.

This report describes the update of the 'River water quality: Heavy metals' indicator using the latest data available for Aotearoa New Zealand. The heavy metals indicator includes two metals that are key indicators of stormwater from urban areas: copper (dissolved) and zinc (dissolved).

This indicator has previously been reported on twice, the first time in 2016 (Gadd 2016) and an update in 2019/2020 (Gadd et al. 2019) using data collected by city councils, regional councils and unitary authorities.

In 2016 water quality state was assessed for a 3-year period from January 2013 to December 2015. The assessment included 17 sites for dissolved copper, located in the Auckland (11 sites) and Wellington (6 sites) regions; and 50 sites for dissolved zinc, located in Auckland (11 sites) and Wellington (7 sites) and Christchurch City (32 sites). Although dissolved copper was measured in Christchurch streams during that period, the detection limit used meant that most data were censored (i.e., below the limit of detection) and state could not be assessed. Trends were assessed over a period of 8 years (from January 2008 to December 2015) at 9 sites in the Auckland region and 5 sites in the Wellington region. In addition, trends in dissolved zinc were assessed at five sites in Auckland for a 20–21-year period.

In 2020 water quality state was assessed for a 3-year period from January 2015 to December 2017. The state assessment included 55 sites for both dissolved copper and dissolved zinc, located in the Auckland (11 sites) and Wellington (5 sites) regions and Christchurch City (39 sites). Trends were assessed over a period of 10 years (from January 2008 to December 2017) at 11 sites in the Auckland region and 7 sites in the Wellington region, and for a 7-year period (January 2011 to December 2017) for 28 sites (for dissolved zinc, only 13 for dissolved copper) in Christchurch City. In addition, trends in dissolved zinc were assessed at five sites in Auckland for a 22-year period.

There are three key differences between those two previous assessments and the assessment reported here:

1. Both of the above reports focussed on streams and rivers that were classified as "urban" only[1], that is, those streams/rivers with more than 15% urban land cover in the upstream catchment as defined by Snelder and Biggs (2002).
2. Both of the above reports included an assessment of other water quality variables.
3. Dissolved copper and dissolved zinc concentrations were compared to guideline values from ANZECC/ARMCANZ (2000).

This report focuses only on dissolved copper and dissolved zinc, as other water quality variables including nutrients, *E. coli*, turbidity, clarity and MCI were reported on in 2022, for data up to

[1] Rural streams were included in the 2020 report in an assessment of relationships between urban land cover and median dissolved copper and zinc concentrations.

December 2020 (Whitehead et al. 2022b). Further, this report extends the assessment to any river or stream where dissolved copper or zinc have been recently measured.

The water quality guidelines used in New Zealand for assessing the potential effects of copper and zinc on aquatic ecosystems (ANZG 2018) are currently being updated. However, these currently exist in draft form only (Anon 2022, Anon 2023) and are not published or approved as ANZG (2018) guideline values. In this report, both the older guideline values (ANZECC/ARMCANZ 2000) and the draft default guideline values are used to assess the state of dissolved copper and zinc.

2 Data acquisition, organisation and processing

2.1 Water quality variables

Copper and zinc are important pollutants in urban streams, transported via stormwater from roads (zinc from tyre wear, copper from brake pad wear), roofs (zinc from galvanised roofing, copper from copper roofing and spouting) and other impervious surfaces (including paved areas around industrial sites). The dissolved forms of these metals are more important for assessing toxicity than the 'total' forms, which include metals attached to particulate material that are less bioavailable (ANZECC/ARMCANZ 2000). Dissolved metals are typically defined as those that pass through a 0.45 µm filter (USEPA 1996). Dissolved copper and dissolved zinc are routinely monitored by some regional councils around New Zealand as part of State of the Environment (SOE) monitoring, and/or by city councils under the monitoring conditions for stormwater network consents.

The water quality guideline values used to assess potential toxicity to aquatic organisms can be modified for metal bioavailability (see section 3.1.4). This requires hardness, dissolved organic carbon (DOC) and/pH data (Anon 2022, Anon 2023, ANZECC/ARMCANZ 2000) and so these three variables were also requested from each council.

2.2 Data acquisition

Although the Land Air Water Aotearoa (LAWA)[2] webservice collates data from regional and unitary councils across New Zealand, that system does not include metals. We therefore requested data directly from councils throughout New Zealand (listed in Table 2-1) based on enquiries that had identified whether dissolved copper or dissolved zinc are currently monitored in their jurisdictions. In some cases, councils supplied only an update of data (e.g., most recent 4 years) as data had already been supplied for previous analyses. In those cases, we then included data previously acquired to provide the complete data set.

Our request included data on metals, the supporting water quality variables (pH, DOC, hardness, calcium and magnesium), quality coding information and site metadata including site codes, site names and geographic coordinates.

Table 2-1 provides a summary of the monitoring data received through our data requests. Note that there may be additional monitoring (ad hoc or regular) undertaken by other councils that were not contacted or that did not respond to our initial queries. Sites with dissolved copper and zinc data were not evenly distributed around the country (Figure 2-1).

[2] https://www.lawa.org.nz/

Table 2-1: Summary of metals monitoring data received from regional and territorial councils. Green shading indicates suitable data available for the time period of interest. This table only includes Councils where data was requested – those not included in this list had previously indicated that they did not have suitable data.

Council	Abbrev.	Monitoring undertaken
Northland Regional Council	NRC	Total Cu/Zn, campaigns only, 16 sites
Auckland Council	AC	Dissolved Cu/Zn, monthly 2009-ongoing, ~38 sites
Waikato Regional Council	WRC	Total and dissolved Cu/Zn; campaigns only, 115 sites
Environment Bay of Plenty Regional Council	EBOP	Dissolved Cu/Zn campaigns only, 11 sites
Gisborne District Council	GDC	Nothing received
Hawkes Bay Regional Council	HBRC	Dissolved Cu/Zn, approx. quarterly 2007-2013, 5 sites
Taranaki Regional Council	TRC	Nothing received
Greater Wellington Regional Council	GWRC	Dissolved Cu/Zn, monthly ~2009-ongoing, 9-17 sites
Nelson City Council	NCC	Metals not monitored in surface waters
Christchurch City Council	CCC	Dissolved Cu/Zn, monthly, 2011-ongoing, 51 sites
Environment Canterbury	ECan	Total & dissolved Cu/Zn, quarterly, ongoing, 10 sites
Otago Regional Council	ORC	Dissolved Cu/Zn, monthly, 2018-ongoing, 6 sites
Environment Southland	ES	Metals not monitored in surface waters

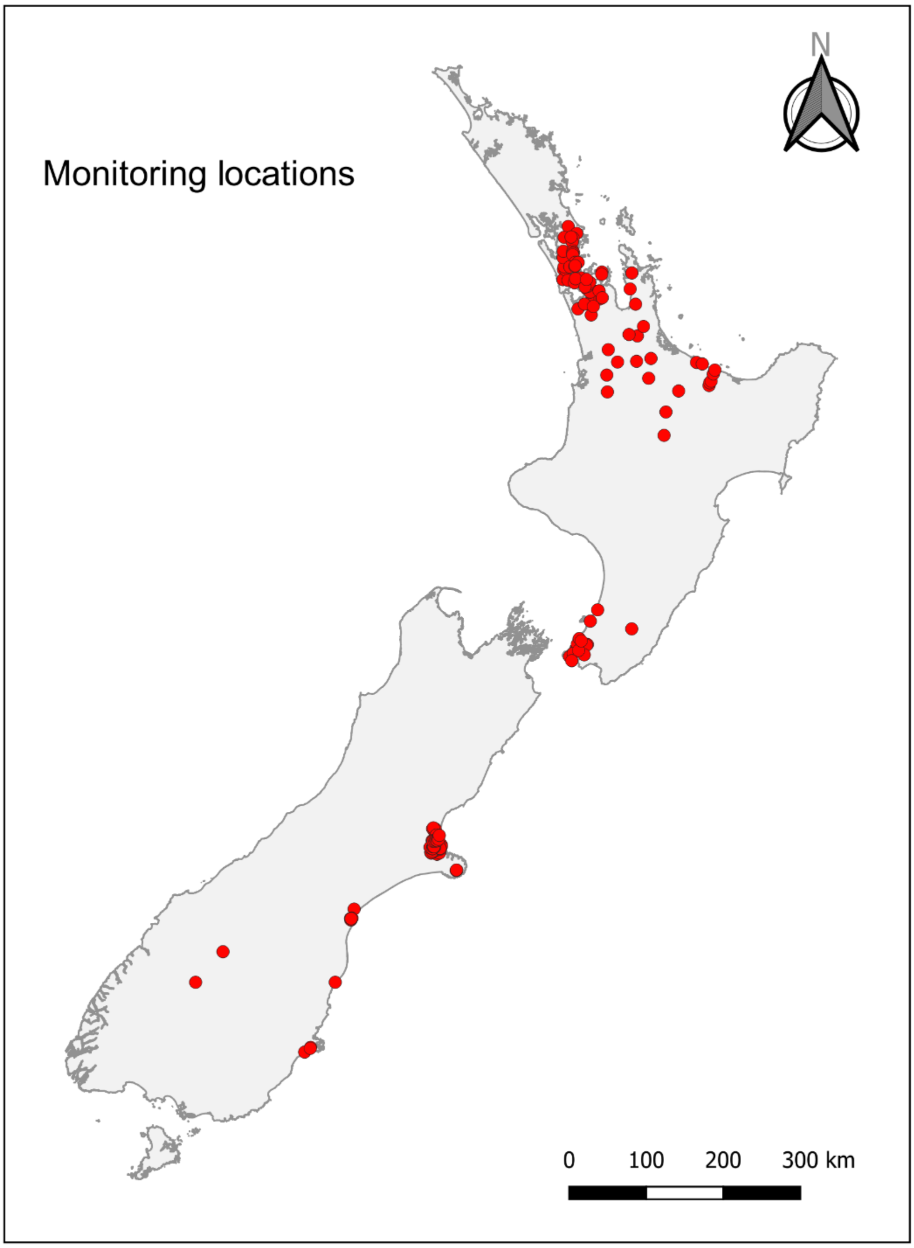


Figure 2-1: Monitoring locations for dissolved zinc and/or dissolved copper that were included in this study.

2.3 Data processing

River water-quality data were processed in several steps to ensure that the datasets acquired from different sources were internally consistent, that site information was complete and accurate, that consistent measurement procedures were used, and that the data were as error-free as possible.

Step 1. Data quality coding. Only data from Auckland Council and Greater Wellington Regional Council were supplied with quality codes that were consistent with the NEMS [3].

[3] see https://www.nems.org.nz/documents/quality-code-schema/

Auckland Council recommended removing data marked as "Excluded". For dissolved copper and zinc this comprised data coded QC400, where samples arrived >96 hours after collection and at >10°C; or where salinity >0.5 ppt indicated a saline influence at the sampling site.

Greater Wellington Regional Council had coded data from July 2021 onwards only. All data coded QC400 were excluded, to be consistent with the screening of Auckland Council data. Prior to July 2021, there was no quality coding, and all those data were retained.

Christchurch City Council do not use NEMS quality coding for their data but had applied their internal quality checks prior to supplying data. All data supplied by CCC were therefore included in the compilation.

Bay of Plenty, Waikato and Otago Regional Councils did not supply NEMS quality coding for their data and all data supplied by these councils were included in the compilation.

Step 2. Reporting conventions. The water-quality data received from councils varied widely in reporting formats, reporting conventions for variable names, site identifiers, date and time formats, units of measurement, and other data structure elements. We first organised data from all sources into a single format. Then we applied a consistent set of reporting conventions. Common errors included mislabelled site-names, incorrect units and data transcription errors. We applied a flagging system developed in the previous project that attaches metadata to individual data points. Flags include censored data (see section 2.5) and assigned units. Dissolved copper and dissolved zinc were consistently reported in units of g/m^3 (as recommended by NEMS (2019)) and therefore no unit conversions were required for these data.

Step 3. Data duplication. In some cases there were multiple samples collected within a month (Auckland), or within a day (Canterbury). In the cases of multiple samples collected on a day, the median value of the measurement was taken (for uncensored data) or, for censored data, the most common censored value. The new value was then assigned a time of midday. For the Auckland data, the duplicates within a month occurred where samples were collected at the start and end of a month, but not collected in the preceding or subsequent month. In these cases, the data were left unchanged for the assessment of state and trends.

Step 4. Comparable field and laboratory methods.

The next data processing step was to assess whether methods used for each variable were comparable. For most of the variables, there were two or more measurement procedures used across the Councils. Table 2-2 lists the most common procedures used for each variable, and the procedures corresponding to data retained for analysis.

Several Councils also (or alternatively) measured total copper and total zinc and/or total recoverable copper and zinc. These measures include the metals attached to particulates and are not comparable to dissolved or soluble forms of metals; those variables were not included in this analysis.

Dissolved organic carbon, hardness and pH are not used for environmental indicators, but were required to adjust dissolved copper and zinc water quality guideline values (see section 3.1.4). Some variation in the analytical methods used for DOC, hardness and pH was allowed to maximise the number of dissolved copper and zinc observations that could be compared to default guideline values. Where hardness was not reported but calcium and magnesium were, hardness was calculated as 2.497 x [Ca] + 4.118 x [Mg] where Ca and Mg are the concentrations of dissolved calcium and magnesium respectively, as measured in mg/L. If it was not clear whether the calcium or magnesium concentrations were dissolved or total, those data were excluded.

Table 2-2: Measurement procedures used by different councils for each water quality variable.

Variable	Measurement procedure(s)	Comments
Copper	Filtration through 0.45 µm membrane filters, ICP-MS (USEPA 200.8) Filtration through GF/F filters (0.7 µm), GFAA Filtration through 0.45 µm membrane filters, ICP-MS (APHA 3125 B, 21st ed. 2005)	All procedures retained, difference in filter pore size expected to result in negligible differences
Zinc	Filtration through 0.45 µm membrane filters, ICP-MS (USEPA 200.8) Filtration through GF/F filters (0.7 µm), ICP-OES Filtration through 0.45 µm membrane filters, ICP-MS (APHA 3125 B, 21st ed. 2005)	All procedures retained, difference in filter pore size expected to result in negligible differences
DOC	Dissolved non-purgeable organic carbon: Acidification, purging to remove inorganic C, super-critical persulphate oxidation at 375°C, IR detection. APHA 5310 C (modified) 23rd ed. 2017 Filtration, acidification, high temperature catalytic oxidation, IR detection. APHA 5310B	All procedures retained, although there may be some differences between methods.
Hardness	Calculation from analysis of dissolved calcium and dissolved magnesium (APHA 2340B) EDTA titrimetric method. APHA Method 2340C	Both procedures retained.
Calcium	Filtered, ICP-MS Filtered, ICP-OES	Both procedures retained.
Magnesium	Filtered, ICP-MS Filtered, ICP-OES	Both procedures retained.
pH	Measured in field by hand-held meter. APHA Method 4500-H+ B Measured in laboratory by meter. APHA Method 4500-H+ B	All procedures retained. Where both methods were used on the same day, the laboratory measurement was used.

Step 4. Error correction and adjustment. We manually inspected the data to correct identifiable errors (e.g., transcription errors, particularly in site names). We used time-series plots for each Council's data set to assess data coverage and presence of censored data. We used data tables and box plots to identify potential outliers for each variable.

2.4 Metadata acquisition and processing

Metadata were required to assess potential drivers of heavy metals in rivers and streams. This first required all sites to be mapped to an "nzsegment" – the identification code for the stream segment that the site is located on, as defined by the digital river network (REC2.4). Most of the councils did not provide nzsegments for the sites with metal data. In some cases these were acquired from the database developed for the recent national state and trends reporting (Whitehead et al. 2022b) by joining based on lawaID – a site identification code associated with the LAWA database. Other sites (where lawaID was not provided) were mapped to the digital river network using an RShiny tool developed by NIWA to assign nzsegments based on the site coordinates. Many of the stream sites were located close to confluences or in locations where the digital network does not accurately match the real river locations. Each site assignment was checked manually to ensure the site was mapped to the correct waterway, based on the site name and topographical map features.

Land cover information were acquired from the Land Cover Database Version 5.0 (LCDB5). The LCDB5 comprises 33 mainland land cover classes, generated from satellite imagery collected in summer 2018/19. The land cover classes included in this analysis were those representing urban land cover, orchards, pastoral farming, and exotic forest. These were coarsened into three key land cover classes, as defined in Table 2-3. In addition, the three coarsened land cover classes were combined to represent "human modified landcover" as defined by Stats NZ[4]. For each site, land cover data were acquired from a dataset recently collated for MfE (Whitehead et al. 2022a) that associated the LCDB5 with the river network and associated catchments as represented by REC2.4.

Table 2-3: Land cover categories and LCDB5 classes used in the assessment of state and trends. .

Coarsened land cover class	LCDB5 classes included	LCDB5 Class Code
Urban	built-up area	1
	urban parkland/open space	2
	transport infrastructure	5
	surface mine or dump	6
Pastoral farming	high producing grassland	40
	short-rotation cropland	30
	orchards, vineyards or other perennial crops	33
Exotic forest	exotic forest	71
	forest-harvested	64

[4] https://datainfoplus.stats.govt.nz/item/nz.govt.stats/0eb0604f-c762-4134-99e7-5da2d250c48a

In addition to calculating the proportion of each coarsened land cover category, each site was assigned to a categorical land cover type. This used the categorical approach used in previous state and trend assessments, based on Snelder & Biggs (2000), with an additional class of "Orchards" at request of Stats NZ. The categorisation of orchards using ≥ 2% was based on an analysis of the distribution of land cover data.

Categories were assigned using the following rules:

- classified as urban if ≥ 15 percent urban landcover in the catchment,
- classified as orchard if ≥ 2 percent landcover in the catchment in the orchards, vineyards or other perennial crops class,
- classified as pastoral if ≥ 25 percent pastoral landcover in the catchment and not already classified urban, and
- otherwise, classified as other.

Data related to impervious surfaces were acquired from Toitū Te Whenua / Land Information NZ via the koordinates data service. Layers representing building outlines[5] and roading polygons[6] were downloaded on 3 April 2023 with publication dates of 27 March 2023 and 31 March 2023 respectively. Building outlines and roading polygons were combined and used as a proxy of upstream catchment impervious surface area. The catchment upstream of each monitoring site was delineated using the digital river network (REC 2.4) and this was used to calculate the sum of the impervious surface area, and the proportion of impervious surface in the upstream catchment.

2.5 Censored values

For dissolved copper and zinc, many observations have concentrations too low to be measured with precision with routine analytical methods. These are considered to be below the analytical "detection limit" for that variable – which corresponds to the lowest concentration that can be measured with acceptable precision. Cases where values of variables are below the detection limit are often indicated by the data entries "<DL", where DL is the laboratory detection limit. These measurements are called censored values.

Although commonly used, replacement of censored values with constant multiples (e.g, half) of the detection limits can result in misleading results when statistical tests are subsequently applied to those data (Helsel 2012).

In this study, different procedures were used to handle censored data in the state and trend analyses, as appropriate for each analysis. The procedure used for state analyses is set out in section 3.1.2, and the procedure used for trend analyses is set out in section 3.2.2.

[5] https://koordinates.com/from/data.linz.govt.nz/layer/101290/
[6] https://koordinates.com/from/data.linz.govt.nz/layer/50796/

3 Analysis methods

3.1 Water quality state analyses

3.1.1 Time period for state analyses

When characterising state based on observed water quality variables, it is general practice to define consistent time periods for all sites and to define the acceptable proportion of missing observations (i.e., data gaps) and how these are distributed across sample intervals so that site grades are assessed from comparable data. The acceptable proportion of missing observations and representation of the distribution of observations across the time period are commonly referred to as site inclusion or filtering rules.

The state assessments were made for the 5-year time period to the end of June 2022. The start and end dates for this period were determined by the availability of data (see section 2.2), MFE reporting periods and consideration of statistical precision of the state statistics. The statistical precision of the state statistics depends on the variability in the water quality observations and the number of observations. For a given level of variability, the precision of a state statistic increases with the number of observations. As a general rule, the rate of increase in the precision of state statistics slows for sample sizes greater than 30 (i.e., there are diminishing returns on increasing sample size with respect to precision above this number of observations, McBride (2005)). In this study, a period of five years represented a reasonable trade-off for evaluating state statistics because it yielded a sample size of 50 or more observations for most sites and is consistent with the latest national river water-quality state analysis (Whitehead et al. 2022b).

Because water quality data tends to exhibit seasonal fluctuations, it is also important that each season is represented over the period of record. For river water quality monitoring in New Zealand, sampling is generally monthly and seasons are defined by months in this assessment. We therefore applied rules that restricted site × variable combinations in the state analyses to those with measurements for at least 80% of the years (four out of five years) and at least 80% of the seasons in the period (48 of 60 months). Site × variable combinations that did not comply with these rules were included in the initial presentation of heavy metal state but were flagged as not meeting the minimum data requirements.

Table 3-1: Number of sites meeting minimum data requirements for three and five year periods for assessing state.

	Copper		Zinc	
Region	**3 years**	**5 years**	**3 years**	**5 years**
Auckland	32	34	32	34
Wellington	10	10	10	10
Canterbury	39	50	39	50
Otago	6	6	6	6

The above are subjective decisions, and therefore in the supplementary files of state we provide state statistic estimates for all sites and variables (irrespective of compliance with the minimum datarequirements) along with appropriate metadata about the number and distribution of samples to allow more stringent or lenient filtering rules to be applied at a later date, as required.

3.1.2 Handling censored values

Censored values were replaced by imputation for the purposes of calculating the statistics. Left censored values (values below the detection limit(s)) were replaced with imputed values generated using ROS (Regression on Order Statistics; Helsel, 2012), following the procedure described in Larned et al. (2015). The ROS procedure produces estimated values for the censored data that are consistent with the distribution of the uncensored values and can accommodate multiple censoring limits. When there are insufficient non-censored data to evaluate a distribution from which to estimate values for the censored observations, censored values are replaced with half of their reported value. There were no right censored values (i.e., above the reporting limit) in the dissolved metal dataset.

3.1.3 Evaluation of state statistics

For each site and variable, we characterised the current state using state statistics[7] (5th, 20th, 25th, 50th, 75th, 80th, and 95th percentiles) derived from the distribution of measured values for the 5 - year period July 2018 to June 2022 (inclusive). All percentiles were calculated using the Hazen method.[8]

3.1.4 Comparisons to water quality guideline values

The water quality guidelines used in New Zealand to assess the effects of toxicants on aquatic ecosystems (ANZG 2018), provide default guideline values (DGVs) based on differing levels of species protection. A 95% level of species protection is recommended for slightly to moderately disturbed ecosystems.

The existing DGVs for dissolved copper and zinc (ANZG 2018) are based on ANZECC/ARMCANZ (2000), and for dissolved zinc these can be modified based on water hardness, as hardness is known to reduce the toxicity of zinc. DGVs for dissolved copper are not modified based on hardness or any other variable.

DGVs for dissolved copper and zinc are currently being updated but exist in draft form only (Anon 2022, Anon 2023). The draft updated DGVs include updates to the methods that account for bioavailability of metals, consistent with international advances. The draft updated zinc DGVs can be adjusted based on the hardness, DOC and pH of the water (Table 3-2). The draft updated copper DGVs can be adjusted based on the concentration of dissolved organic carbon (DOC) in the water. Although only in draft form, these DGVs are used in this report as the best information available at this point in time for assessing the potential effects from copper and zinc toxicity.

The collated dissolved copper and zinc concentration data were compared to DGVs. If relevant (see Table 3-2), the DGV was first adjusted based on the modifying factors (either DOC, or hardness, or DOC, hardness and pH) as measured in each sample. In some cases, the DOC, hardness or pH were outside the applicable range for adjustment and if so, a DGV could not be calculated and the measured concentrations could not be compared to DGVs.

[7] In Lake and rive water quality state assessments for which there are prescribed attribute states, 'state statistics' are referred to as 'compliance statistics'.
[8] (http://www.mfe.govt.nz/publications/water/microbiological-quality-jun03/hazen-calculator.html) Note that there are many possible ways to calculate percentiles. The Hazen method produces middle-of-the-road results (McBride 2005, chapter 8) and is method that has been previously used for assessing water quality state (e.g., Gadd (2016), Gadd et al. (2019), Whitehead et al. (2022)).

Table 3-2: Guideline values used to assess copper and zinc in this report. DGV = default guideline value

Variable	Guideline source	GV (µg/L)	GV modifiers	Modification procedure
Copper	ANZECC/ARMCANZ (2000)	1.4	None	Not applicable
	Anon (2023)	0.47	DOC	$Adjusted\ DGV = 0.47 \times \left(\frac{DOC}{0.5}\right)^{0.977}$
Zinc	ANZECC/ARMCANZ (2000)	8	Hardness (H)	$Adjusted\ DGV = 8 \times \left(\frac{H}{0.5}\right)^{0.85}$
	Anon (2022)	4.1 *	DOC, pH and hardness	Algorithm based on multiple linear regressions, implemented in R

Note: * Draft guideline value at pH 7.5, hardness of 30 mg $CaCO_3$ /L and DOC of 0.5 mg/L.

3.1.5 Relationships between water quality state and catchment land cover

We used linear regressions to relate water-quality state to various possible explanatory variables:

- urban land cover,
- human-modified land cover,
- impervious surface area, and
- orchards and vineyards as a specific land use

Linear regression models were fitted with each of these explanatory variables separately. The dissolved copper and dissolved zinc concentrations were first log-transformed for the linear regression so that the residuals were approximately normally distributed. Linear regressions were undertaken using the R statistical computing software (R Core Team, 2023) with the packages ggplot2 (Wickham 2016) and ggpubr (Kassambara 2022) to display data.

3.2 Water quality trend analyses

3.2.1 Sampling dates, seasons and time periods for analysis

In trend assessments, there are several reasons why it is important to define the trend period and seasons and to assess whether the observations are adequately distributed over time. First, because variation in many water quality variables is associated with the time of the year or "season", the robustness of trend assessment is likely to be diminished if the observations are biased to certain times of the year. Second, a trend assessment will always represent a time period; essentially that defined by the first and last observations. The assessment's characterisation of the change in the observations over the time period will not be robust if the observations are not reasonably evenly distributed across the time period. For these reasons, important steps in the data compilation process include specifying the seasons, the time period, and ensuring adequately distributed data.

Monitoring programs are generally designed to sample with a set frequency, (e.g., monthly, quarterly). The trend analysis 'season' is generally specified to match this sampling frequency (e.g., seasons are months, or quarters). There is therefore generally an observation for each sample interval (i.e., each season, such as month or quarter, within each year).

Two common deviations from the prescribed sampling regime are (1) the collection of more than one observation in a sample interval (e.g., two observations within a month) and (2) a change in sampling interval within the time period. Both of these deviations occurred in the dissolved metals datasets, particularly type (2), where sampling frequencies have changed in some regions (from quarterly to monthly) over the observation record. Type (1) deviations only occurred within the Auckland data and these "duplicates" were offset by no samples in the next month and so all data were retained for the trend analysis.

For type (2) deviations, we coarsened the sampling interval to define seasons to match the part of the record with the lower sampling frequency. This was achieved by taking the observation in the higher frequency part of the record that was closest to the midpoint of the seasons defined by the coarser part of the record. The reason for not using the median value in this case is that it will induce a trend in variance, which will invalidate the distributional assumptions of the Mann Kendall S test statistic (Helsel et al. 2020).

The trend for all site and variable combinations was characterised by the rate of change of the central tendency of the observations through time. Because water quality is constantly varying through time, the evaluated rate of change depends on the time-period over which it is assessed (Whitehead et al. 2022b). Therefore, trend assessments are specific for a given period of analysis.

For a national study that aims to allow robust comparison of trends between sites and to provide a synoptic assessment of trends across the whole country, such as the present study, it is important that the trends evaluated at each site are commensurate in terms of their statistical power and representativeness of the time period. In these types of studies, it is general practice to define consistent time periods (i.e., trend duration and start date) so that all sites are subjected to the same conditions (i.e., equivalent political, climate, economic conditions). It is also general practice to define the acceptable proportion of gaps and how these are distributed across sample intervals so that the reported trends are assessed from comparable data.

There are no universally agreed data requirements or filtering rules for trend assessments performed over many sites and variables such as the present study. Defining filtering rules for minimum data requirements is complicated by a trade-off: more restrictive rules increase the robustness of the individual trend analyses but will generally exclude a larger number of sites than lenient rules, thereby reducing spatial coverage. In general, this trade-off is also affected by the duration of trend period. Progressive growth in regional council monitoring effort over time means that shorter and more recent trend periods will generally have a larger number of eligible sites.

The application of filtering rules for variables that are measured at monthly or quarterly intervals requires two steps. First, retain sites for which observations are available for at least *X*% of the years in the time period. Second, retain sites for which observations are available for at least *Y*% of the sample intervals.

In this study, we used filtering rules applied by Larned et al. (2018), which set both X and Y to 80%. It is noted that the filtering rules for imply a tolerance of variable levels of statistical power and temporal representativeness across the sites that were included in the analysis.

The trends presented in this study were for 10-year periods ending at 31 December 2022. In the supplementary information we have additionally included trend assessments for the maximum record length. This was to provide some information about trends at the sites that have been established in recent past, which have short records (i.e., < 10 years), and also to evaluate the longest possible trend period at sites that have been operating for longer than 10 years. We made two exceptions for the identification and calculation of maximum possible trend period. First, for sites in the Auckland region, for both copper and zinc, we did not allow the starting date to be earlier than 2006, as a large majority of observations prior to this date were classified as censored due to a very high detection limit, whereas after this date a much lower detection limit was in place, allowing more information about trend to be evaluated. Secondly, for sites monitored by Christchurch City Council, we did not allow the starting date to be earlier than 2017 for dissolved copper, as a large majority of observations prior to this date were classified as censored due to a higher detection limit, whereas after this date a much lower detection limit was in place, allowing more information about trend to be evaluated.

We advise caution with the interpretation of trends for time periods shorter than 10 years. It has been demonstrated that the shorter the time period over which a river water quality trend is assessed, the greater the level of influence of climatic variation on the assessed trend (Snelder, Fraser, Larned, Monaghan, *et al.*, 2021).

3.2.2 Handling censored values

Censored values are managed in a special way by the non-parametric trend assessment methods described in section 3.2.4. It is therefore important that censored values are correctly identified in the data. Detection limits or reporting limits that have changed through the trend time period (often due to analytical changes) can induce trends that are associated with the changing precision of the measurements rather than actual changes in the variable. This possibility needs to be accounted for in the trend analysis and this is another reason that it is important that censored values are correctly identified in the data.

We applied a “high-censor” filter in the trend assessments to minimise biases that might be introduced due to changes in detection limits through the trend assessment period. The high-censor filter identifies the highest detection limit for each water quality variable in the trend assessment period (or some nominated highest detection limit) and replaces all observations below this level with the highest detection limit and identifies these as censored values.

The water quality datasets included a small number of left censored values that were much larger than the apparent detection limit at any given time (outliers). Unsupervised application of the high-censor filter in these circumstances can lead to the unnecessary loss of statistical power in the assessment. To avoid this problem, we employed the following approach. We expected that systematic changes in detection limit would be relatively consistent for a variable across a monitoring domain (i.e., within a site). To explore patterns in detection level, we plotted left censored data over time by variable and region and used these plots to identify the occurrence of outliers. We identified a maximum realistic detection level for each variable and region and capped the high-censor level at these values.

3.2.3 Seasonality assessment

For many site/variable combinations, observations vary systematically by season (e.g., by month or quarter). In cases where seasons are a major source of variability, accounting for the systematic seasonal variation should increase the statistical power of the trend assessment (i.e., increase the confidence in the estimate of direction and rate of the trend). The purpose of a seasonality assessment is to identify whether seasons explain variation in the water quality variable. If this is true, then it is appropriate to use the seasonal versions of the trend assessment procedures at the trend assessment step (Section 3.2.4).

We evaluated seasonality using the Kruskall-Wallis multi-sample test for identical populations. This is a non-parametric ANOVA that determines the extent to which season explains variation in the water quality observations. Following Hirsch *et al*. (1982), we identified site/variable combinations as being seasonal based on the *p*-value from the Kruskall-Wallis test with α=0.05. For these sites/variable combinations, subsequent trend assessments followed the "seasonal" variants, described in section 3.2.4.

The choice of α is subjective and a value of 0.05 is associated with a very high level of certainty (95%) that the data exhibit a seasonal pattern. In our experience there are generally diminishing differences between the seasonal and non-seasonal trend assessments for *p*-values values larger than 0.05 (Helsel et al. 2020).

3.2.4 Analysis of trends

The purpose of trend assessment is to evaluate the direction (i.e., increasing or decreasing) and rate of the change in the central tendency of the observed water quality values over the period of analysis (i.e., the trend). Because the observations represent samples of the water quality over the period of analysis, there is uncertainty about the conclusions drawn from their analysis. Therefore, statistical models are used to determine the direction and rate of the trend and to evaluate the uncertainty of these determinations.

We have evaluated trends using the LWPTrends functions (Snelder & Fraser 2021) that are implemented in the R statistical computing software (R Core Team 2023s). A brief description of the theoretical basis for these functions is described below.

Trend direction assessment

The trend direction and the confidence in the trend direction were evaluated using either the Mann Kendall assessment or the Seasonal Kendall assessment. Although the non-parametric Sen slope regression also provides information about trend direction and its confidence, the Mann Kendall assessment is recommended, rather than Sen slope regression, because the former more robustly handles censored values. However, Sen slope regression is the recommended method for assessing the trend rate (see next section).

The Mann Kendall assessment requires no *a priori* assumptions about the distribution of the data but does require that the observations are randomly sampled and independent (no serial correlation) and that there is a sample size of ≥ 8. Both the Mann Kendall and Seasonal Kendall assessments are based on calculating the Kendall *S* statistic, which is explained diagrammatically in Figure 3-1.

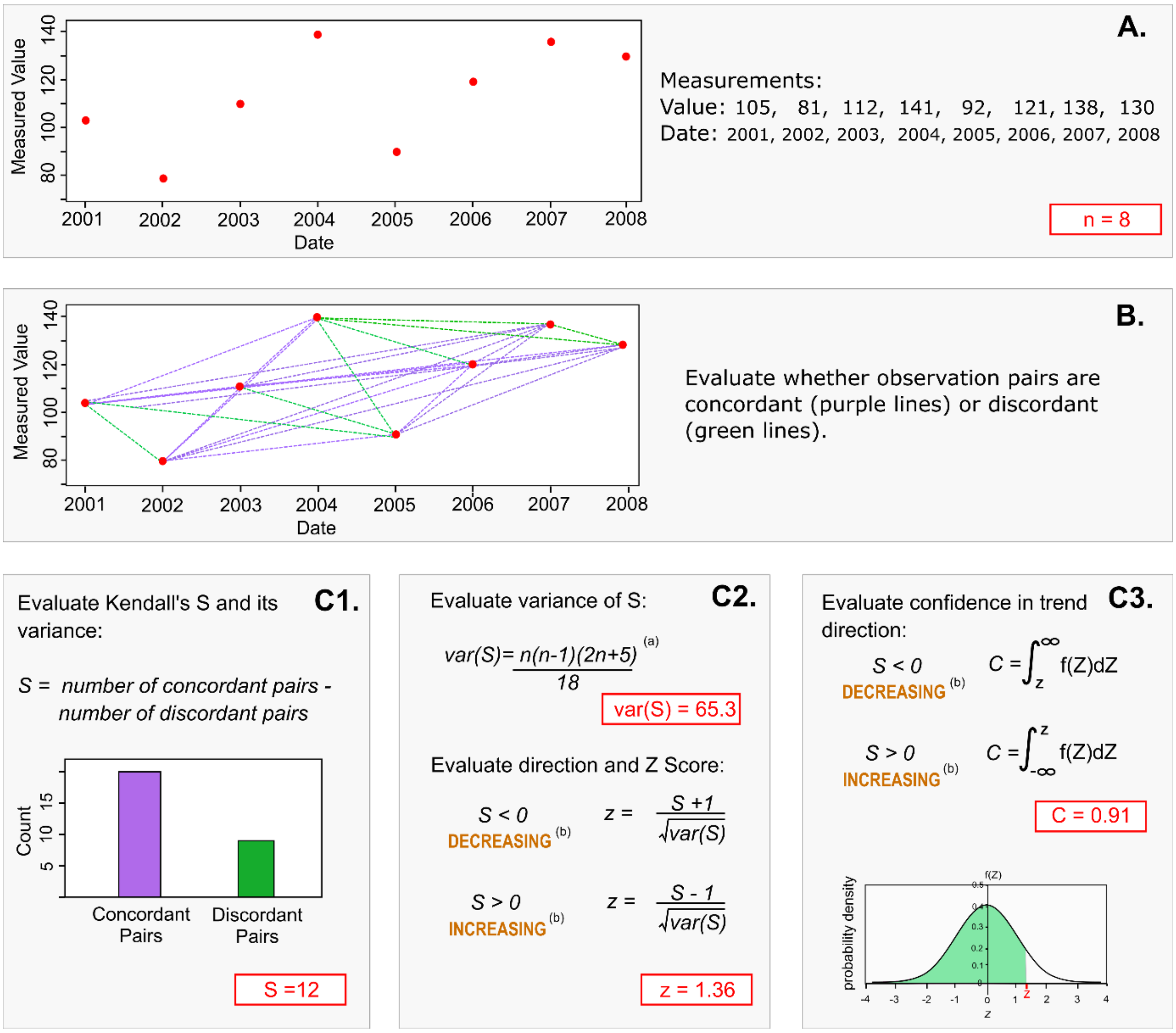


Figure 3-1. Pictogram of the steps taken in the trend direction assessment to calculate the Kendall S statistic and its confidence in trend direction. Notes: [a] the calculation of the variance in S has some adjustments to account for ties (numerically equal values) and censored values. Details of these adjustments can be found in Helsel (2005, 2012). [b] There is a third alternative, where S=0. In this case C is 0.5, and the trend direction is classified as "indeterminate". Values of S equal to -1 or 1 will also result in a Z value of 0, a p-value of 1 and a C value of 0.5 and the trend direction is similarly classified as "indeterminate".

The Kendall *S* statistic is calculated by first evaluating the differences between all pairs of water quality observations (Figure 3-1, A and B). Positive differences are termed 'concordant' (i.e., the observations increase with increasing time) and negative differences are termed 'discordant' (i.e., the observations decrease with increasing time). The Kendall *S* statistic is the number of concordant pairs minus the number of discordant pairs (Figure 3-1, C1). The water quality trend direction is indicated by the sign of *S* with a positive or negative sign indicating an increasing or decreasing trend, respectively (Figure 3-1, C2).

The seasonal version of the Kendall *S* statistic *S* is calculated in two steps. First, for each season, the *S* statistic is calculated in the same manner as shown in Figure 3-1 but for data pertaining to observations in each individual season. Second, *S* is the sum of values over all seasons ($S = \sum_1^n S_i$), where S_i is the number of concordant pairs minus the number of discordant pairs in the i^{th} season and n is the number of seasons. The variance of *S* is calculated for each season and then summed over all seasons.

The sign (i.e., + or -) of the *S* statistic calculated from the sample represents the best estimate of the population trend direction but is uncertain (i.e., the direction of the population trend cannot be known with certainty). A continuous measure of confidence in the assessed trend direction can be determined based on the posterior probability distribution of S, the true (i.e., population) difference in concordant and discordant pairs (Snelder et al. 2022a). The posterior probability distribution of *S* is given by a normal distribution with mean of *S* and variance of *var(S)*. The confidence in assessed trend direction can be evaluated as the proportion of the probability distribution that has the same sign as S.

In practice confidence can be calculated by first transforming the value of $S = 0$ on the posterior probability distribution into a standard normal deviate, Z (panel C2). *C* is then calculated as area under the standard normal distribution to the left (Z>0) or right (Z<0) of the value of Z, using the quantile function for the normal distribution

The value C can be interpreted as the probability that the sign of the calculated value of *S* indicates the direction of the population trend (i.e., that the calculated trend direction is correct). The value C ranges between 0.5, indicating the sign of *S* is equally likely to be in the opposite direction to that indicated by the true trend, to 1, indicating complete confidence that the sign of *S* is the same as the true trend.

As the size of the sample (i.e., the number of observations) increases, confidence in the trend direction increases. When the sample size is very large, C can be high, even if the trend rate is very low. It is important therefore that C is interpreted correctly as the confidence in direction and not as the importance of the trend. As stated at the beginning of this section; both trend direction and the trend rate are relevant and important aspects of a trend assessment.

Assessment of trend rate

The method used to assess trend rate is based on non-parametric Sen slope regressions of water quality observations against time. The Sen slope estimator (SSE; Hirsch *et al.,* 1982) is the slope parameter of a non-parametric regression. SSE is calculated as the median of all possible inter-observation slopes (i.e., the difference in the measured observations divided by the time between sample dates; Figure 3-2).

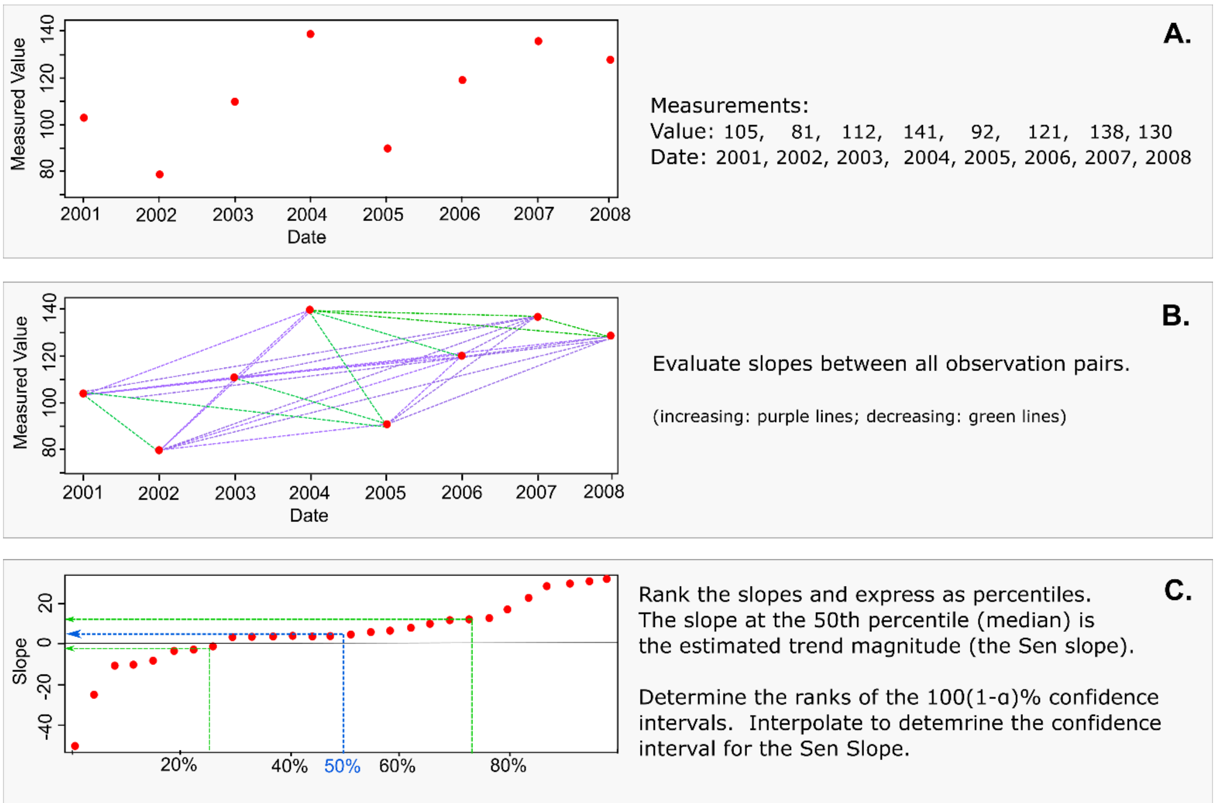


Figure 3-2. Pictogram of the calculation of the Sen slope, which is used to characterise trend rate.

The seasonal Sen slope estimator (SSSE) is calculated in two steps. First, for each season, the median of all possible inter-observation slopes is calculated in same manner as shown in Figure 3-2 but for data pertaining to observations in each individual season. Second, *SSSE* is the median of the seasonal values.

Uncertainty in the assessed trend rate is evaluated following a methodology outlined in Helsel and Hirsch (2002). To calculate the 100(1-α)% two-sided symmetrical confidence interval about the fitted slope parameter, the ranks of the upper and lower confidence limits are determined, and the slopes associated with these observations are applied as the confidence intervals.

The inter-observation slope cannot be definitively calculated between any combination of observations in which either one or both observations comprise censored values. Therefore, it is usual to remove the censor sign from the reported laboratory value and use just the 'raw' numeric component (i.e., <1 becomes 1) multiplied by a factor (such as 0.5 for left-censored and 1.1 for right-censored values). This ensures that in the Sen slope calculations, any left-censored observations are always treated as values that are less than their 'raw' values and right censored observations are always treated as values that are greater than their 'raw' values. The inter-observation slopes associated with the censored values are therefore imprecise (because they are calculated from the replacements). However, because the Sen slope is the median of all the inter-observation slopes, the Sen slope is unlikely to be affected by censoring when a small proportion of observations are censored. As the proportion of censored values increase, the probability that the Sen slope is affected by censoring increases. The outputs from the trend assessment provide an 'analysis note' to identify Sen Slopes where one or both of the observations associated with the median inter-observation slope is censored.

Interpretation of trends

The trend assessment procedure used here facilitates a more nuanced inference than the 'yes/no' output corresponding to the chosen acceptable misclassification error rate. The confidence in direction (C) can be transformed into a continuous scale of confidence the trend was decreasing (C_d). For all trends with $S < 0$, $C_d = C$, and for all $S > 0$ a transformation is applied so that $C_d = 1\text{-}C$. C_d ranges from 0 to 1.0. When C_d is very small, a decreasing trend is highly unlikely, which because the outcomes are binary, is the same as an increasing trend is highly likely.

We used the categorisation of confidence in trend direction used by LAWA to present our results. Each site trend was assigned to a category by firstly, converting C_d into a confidence that a trend was improving (C_i). Improvement is indicated by decreasing trends for all the water quality variables in this study ($C_i = C_d$) except for the macroinvertebrate metrics, visual clarity, Secchi depth and dissolved oxygen (for which increasing trends indicate improvement). For these variables, C_i is the complement of C_d (i.e., C_i=1-C_d). We secondly assigned each site/variable combination to a confidence in trend direction category according to its evaluated confidence of improvement and the categories shown in Table 3-3.

The aggregate proportion of sites in each category shown in Table 3-3 were calculated for sites and for each variable and these values were plotted as colour coded bar charts. These charts provide a graphical representation of the proportions of improving and degrading trends at the levels of confidence indicated by the categories.

Table 3-3: Level of confidence categories used to convey trend confidence and direction.

Categorical level of trend confidence and direction	Value of C_i (%)
Very likely improving	0.90–1.00
Likely improving	0.67–0.90
Low confidence in direction	0.33–0.67
Likely degrading	0.10–0.33
Very likely degrading	0.0–0.10

Outputs from the trend analyses were also classified into four direction categories: improving, degrading, indeterminate, and not analysed. An increasing or decreasing trend category was assigned based on the sign of the S statistic from the Mann Kendall test. An indeterminate trend category was assigned when the Z score equalled zero. Trends were classified as "not analysed" for two reasons:

1) When a large proportion of the values were censored (data has <5 non-censored values and/or <3 unique non-censored values). This arises because trend analysis is based on examining differences in the value of the variable under consideration between all pairs of sample occasions. When a value is censored, it cannot be compared with any other value and the comparison is treated as a "tie" (i.e., there is no change in the variable between the two sample occasions). When there are many ties there is little information content in the data and a meaningful statistic cannot be calculated.

2) When there is no, or very little, variation in the data because this also results in ties. This can occur because laboratory analysis of some variables has low precision (i.e., values have few or no significant figures). In this case, many samples have the same value, and this then results in ties.

4 Results – river state

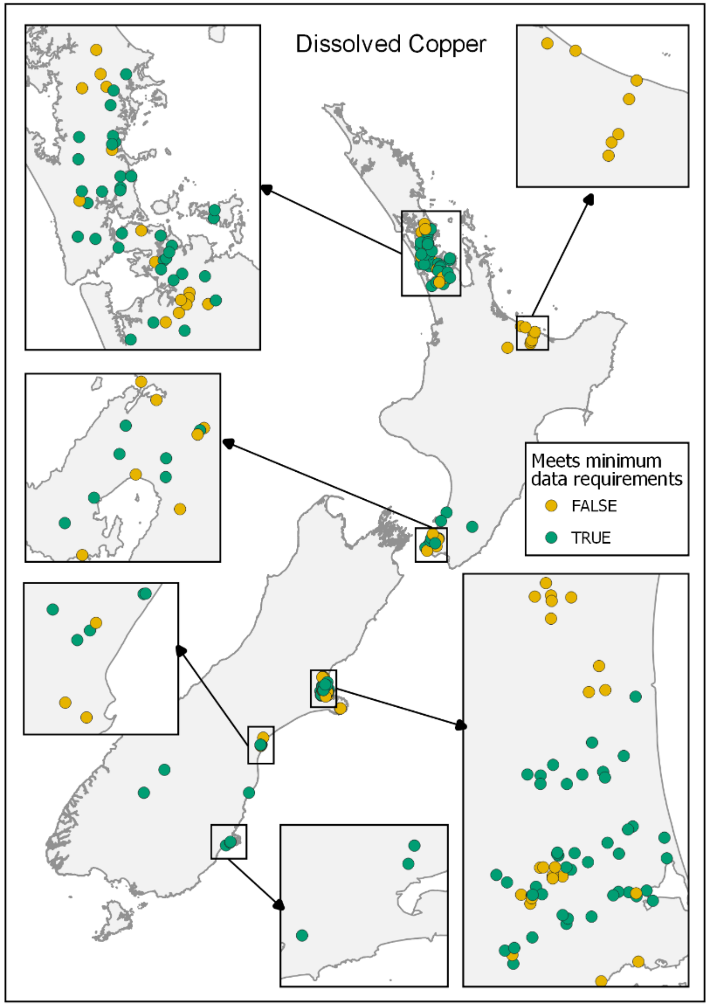
4.1 Data assessed

The number of river monitoring sites that met the minimum data requirements for the state analysis was 100 for each of dissolved copper and dissolved zinc (Table 4-1). There were also data for an additional 59 sites for dissolved copper and 73 sites for dissolved zinc that did not meet the minimum data requirements (Table 4-1).

The geographic distribution of all sites, including those that did not meet the minimum data requirements is shown in Figure 4-1. The sites are poorly distributed across the country and predominantly clustered in the cities. The complete set of state analysis results is provided in the supplementary file "StateResults_withMetadata.csv".

Table 4-1: Number of river monitoring sites by region that were included in the state analyses of dissolved copper and dissolved zinc..

Region	Dissolved copper		Dissolved zinc	
	Met filtering rules	Additional sites	Met filtering rules	Additional sites
Auckland	34	17	34	17
Waikato	None	None	None	16
Bay of Plenty	None	8	None	6
Wellington	10	7	10	7
Canterbury	50	27	50	27
Otago	6	None	6	None
Total	**100**	**59**	**100**	**73**



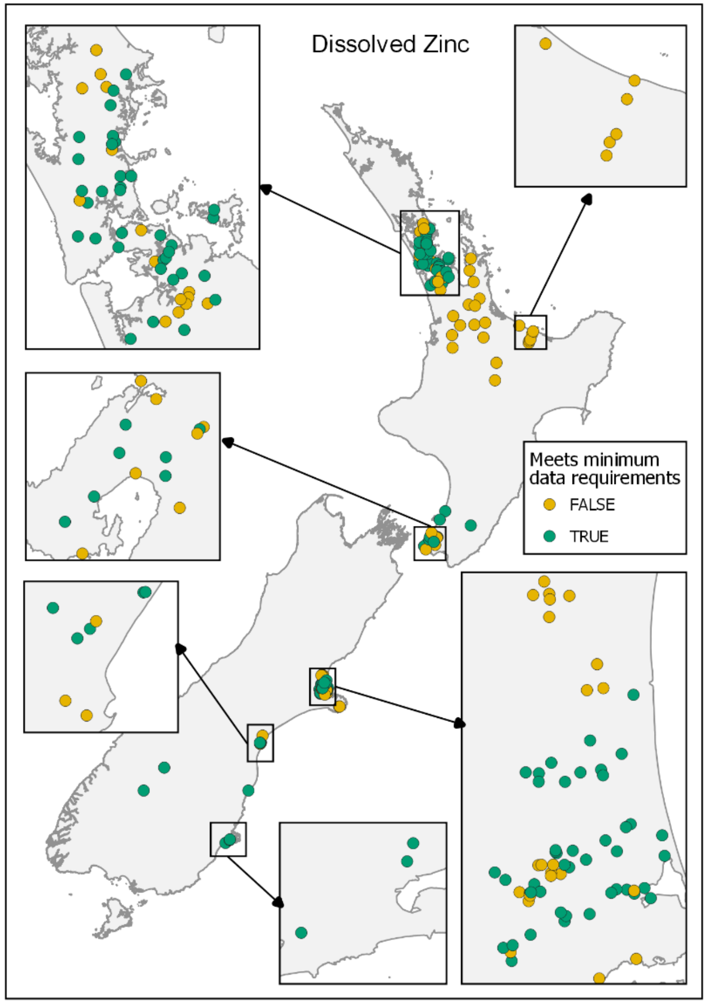


Figure 4-1: Locations of sites where state was evaluated for copper (left) and zinc (right). Sites are coloured based on whether they met the minimum data requirements described in section 3.1.1.

4.2 Median and 95th percentiles

The distributions of site-median values of dissolved zinc and copper for the 2018-2022 period are summarised by region in boxplots (Figure 4-2). These plots include the sites that did not meet minimum data requirements to provide the most comprehensive information on dissolved copper and zinc in New Zealand rivers and streams. The plots indicate that water quality state (i.e., site medians) varies between sites by nearly two orders of magnitude for dissolved copper and more than three orders of magnitude for dissolved zinc.

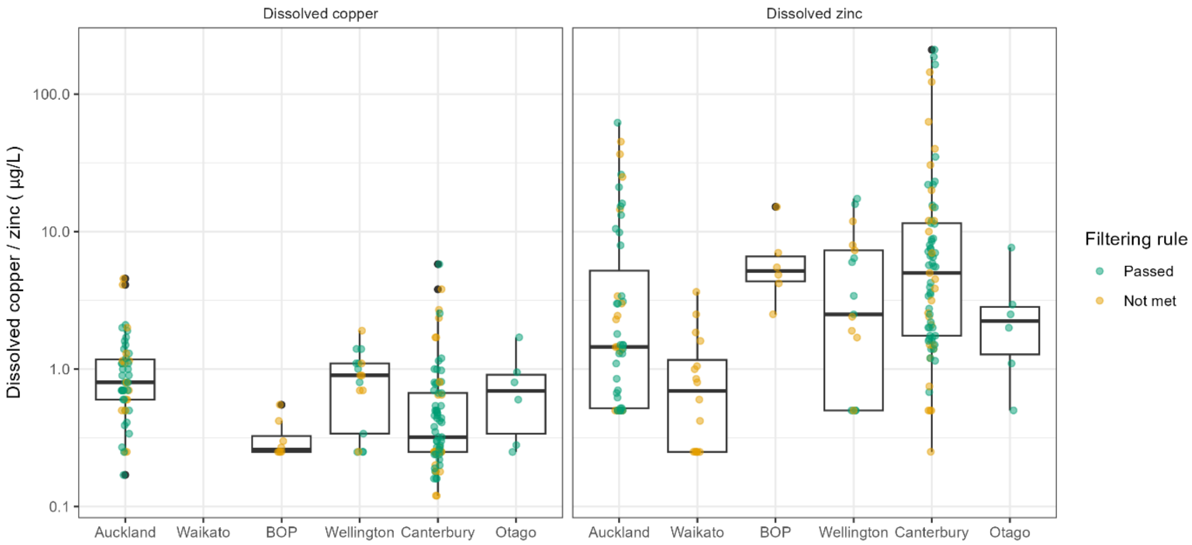


Figure 4-2: Comparison of dissolved copper and zinc concentrations between regions, including sites that did not meet minimum data requirements to provide a comprehensive assessment. Site median concentration shown by point. Boxes represent distribution of data in each region: horizontal line in each box indicates the median of site medians, box indicates the inter-quartile range of medians, whiskers indicate the 5th and 95th percentiles of medians. Individual site medians indicated by dots in green (where filtering rule was passed) and orange (failed filtering rule).

The distributions of the data at each site for both copper and zinc are also shown as rank plots (Figure 4-3). This shows the wide range that can be measured at each site, and hence the need to have many samples to accurately establish a median concentration. From here on, only sites that met the filtering rules are presented.

Figures 4-3 and 4-4 map the median and 95th percentiles for dissolved copper and dissolved zinc. Generally the higher concentrations are found in the urban centres with lower concentrations found around peri-urban areas (see inset maps for Auckland and Christchurch). Relationships between metal concentrations and catchment land use are explored further in section 4.4.

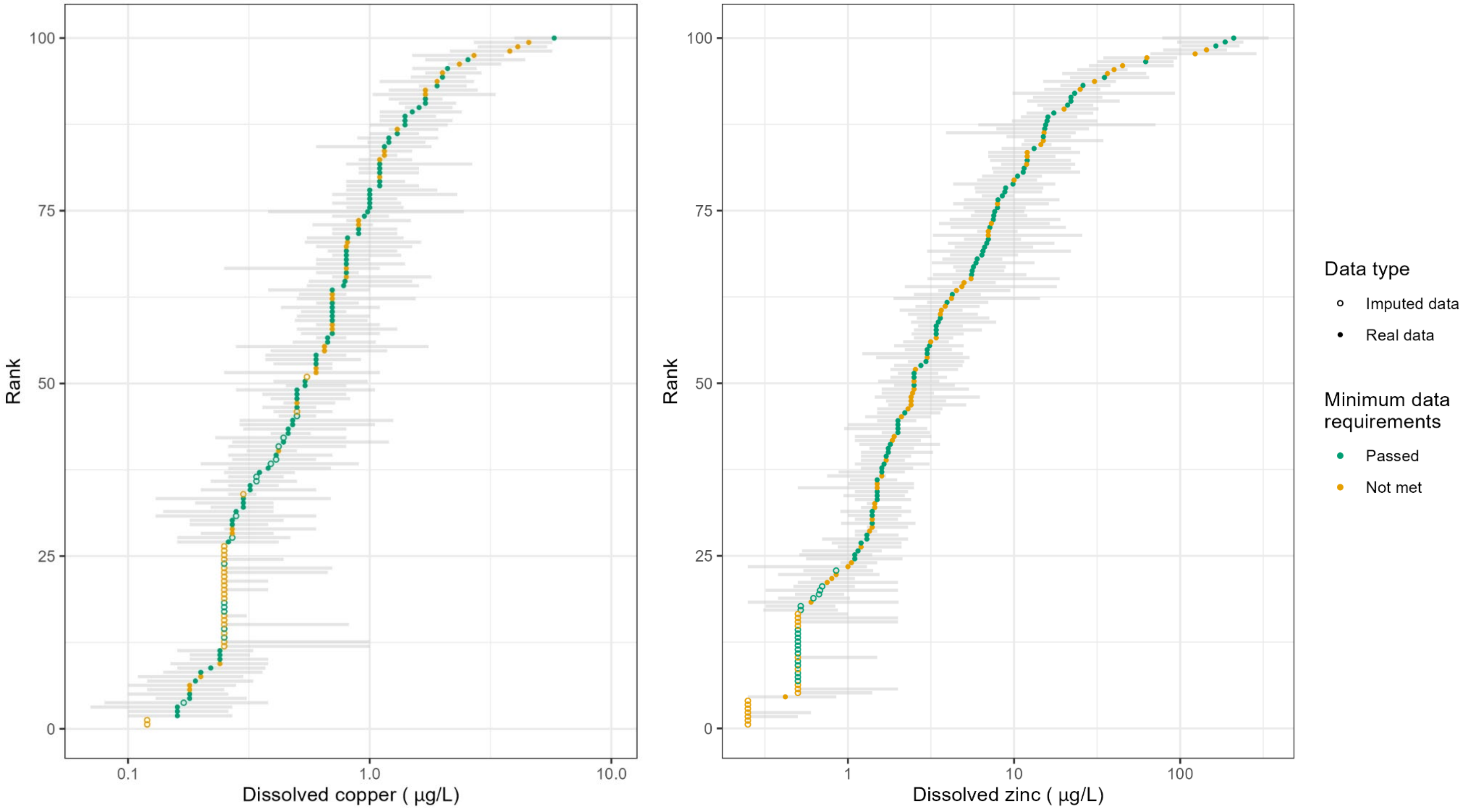
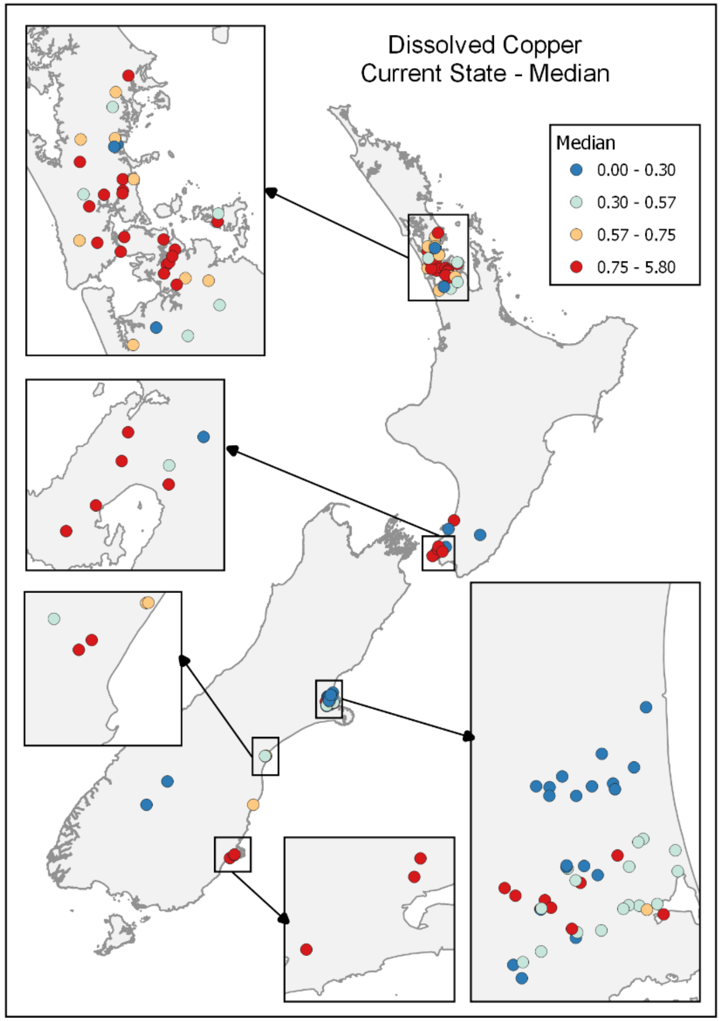


Figure 4-3: Distribution of dissolved copper (left) and dissolved zinc (right) concentrations across all sites assessed. Site median concentration shown by point, grey bars indicates range at each site (25^{th} to 75^{th} percentiles). Colour of point indicates whether the site data met the minimum data requirements for assessment of state – green points met the rule whereas orange points did not. Open circles indicate where the median was based on an imputed value due to more than 50% of data being below the detection limit.



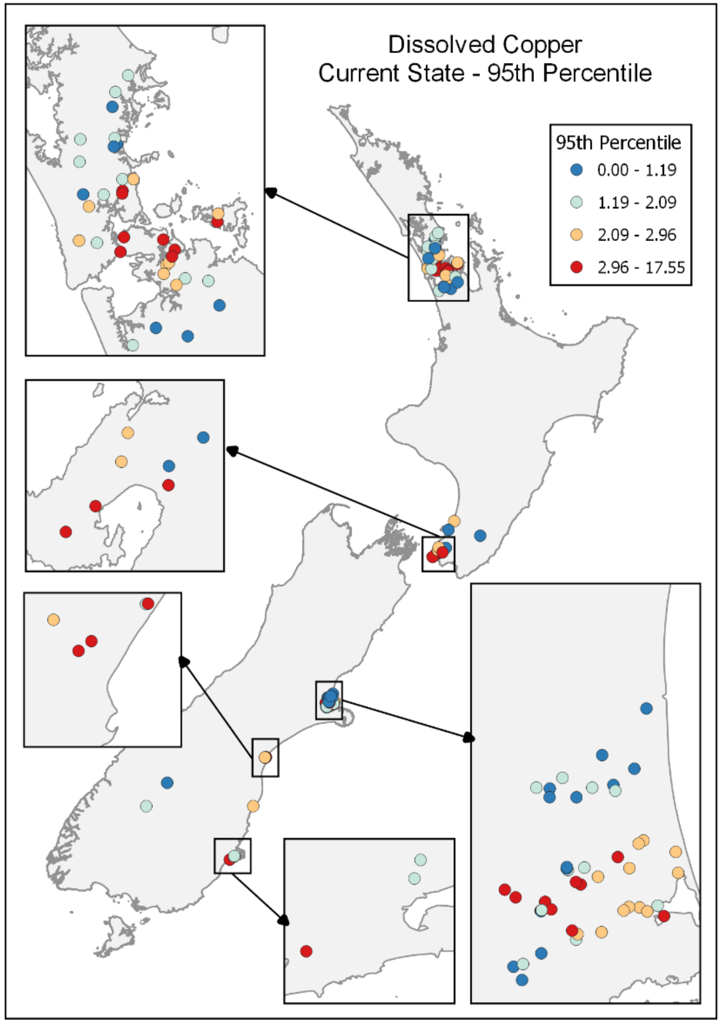


Figure 4-4: Dissolved copper current state based on median (left) and 95th percentile (right) observations. Legend breaks represent the national quantiles for each statistic. Only sites that met the minimum data requirements are shown on the maps.

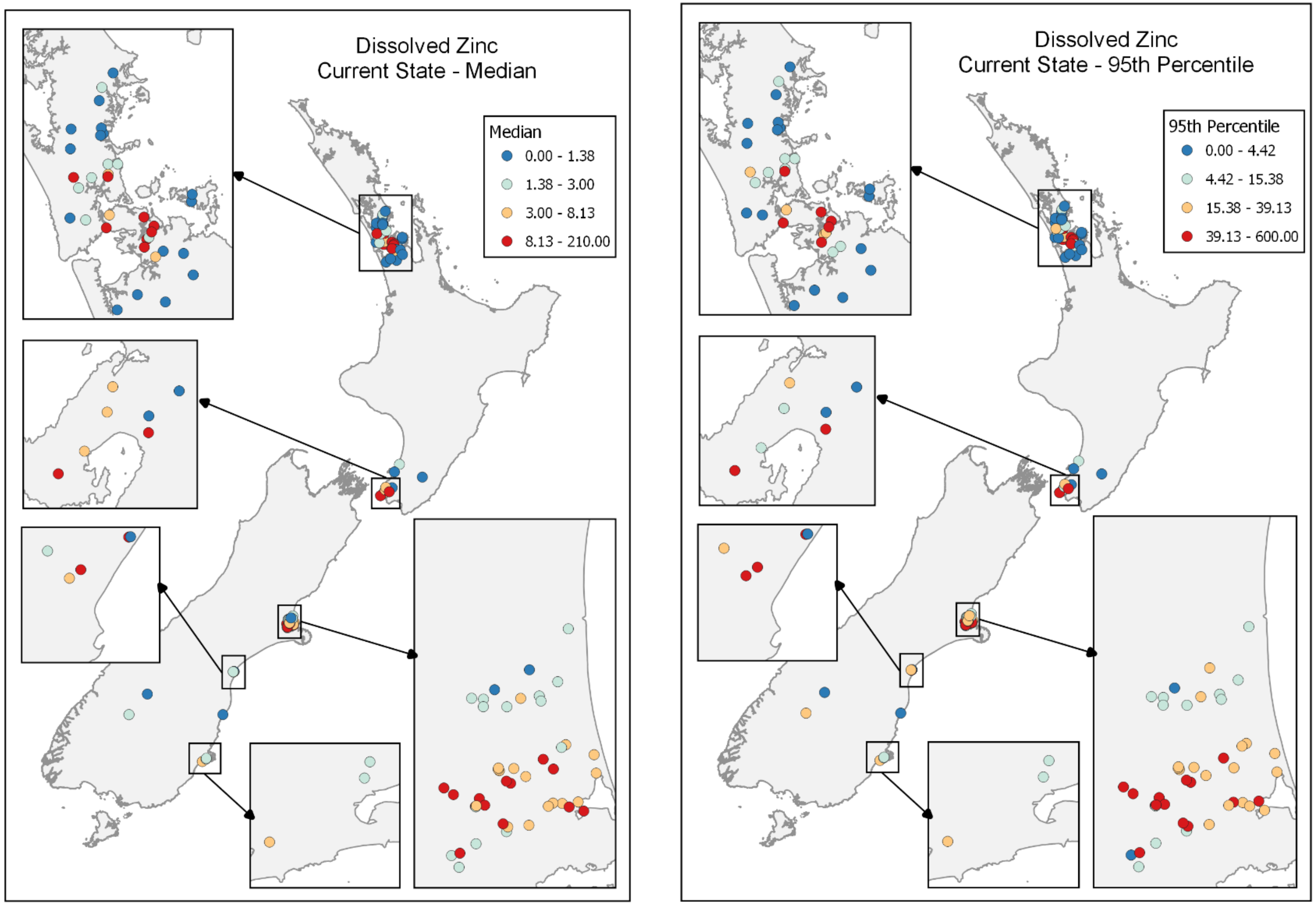


Figure 4-5: Dissolved zinc current state based on median (left) and 95th percentile (right) observations. Legend breaks represent the national quantiles for each statistic. Only sites that met the minimum data requirements are shown on the maps.

4.3 Comparison to guideline values

Table 4-2 provides the number of sites within each region that were compared to the default guideline values (DGVs) for dissolved copper and dissolved zinc. Data from all sites in Auckland and Otago, and most in Wellington were able to be compared to both the ANZECC/ARMCANZ (2000) and the draft DGVs, but there were 16 sites in the Canterbury region that could not be compared to the draft DGVs for dissolved copper or zinc due to an absence of dissolved organic carbon (DOC) data. Furthermore, of the remaining 44 sites in Canterbury and the 6 sites in Otago that were compared to the draft DGVs, these comparisons were possible only for around 15-50% of the samples, as either hardness and/or DOC were not measured on all occasions, or (in a small number of cases) were outside the range of application for the guideline values.

Table 4-2: Summary of the number of sites by region that had sufficient data to be compared to default guideline values for dissolved copper and dissolved zinc..

Region	Dissolved copper		Dissolved zinc	
	ANZECC/ARMCANZ (2000) DGVs	Draft DGVs	ANZECC/ARMCANZ (2000) DGVs	Draft DGVs
Auckland	34	34	34	34
Wellington	10	9	10	9
Canterbury	50	44	50	44
Otago	6	6	6	6
Total	**100**	**93**	**100**	**93**

There were many sites where dissolved copper or zinc exceeded the DGVs on at least one occasion (Figure 4-6). The highest percentage of exceedance of the DGVs were for the sites with urban land cover upstream, particularly for dissolved zinc. For dissolved copper, there were generally fewer samples exceeding the draft updated DGVs than the ANZECC/ARMCANZ (2000) DGVs, however it is possible that this is due to the unavailability of DOC data for those samples with higher dissolved copper concentration, particularly for the sites categorised as pastoral.

The assessment indicates that regardless of the guidelines used, sites in streams categorised as urban regularly exceed both copper and zinc DGVs, whereas at sites in other land cover categories, there is lower levels of exceedance.

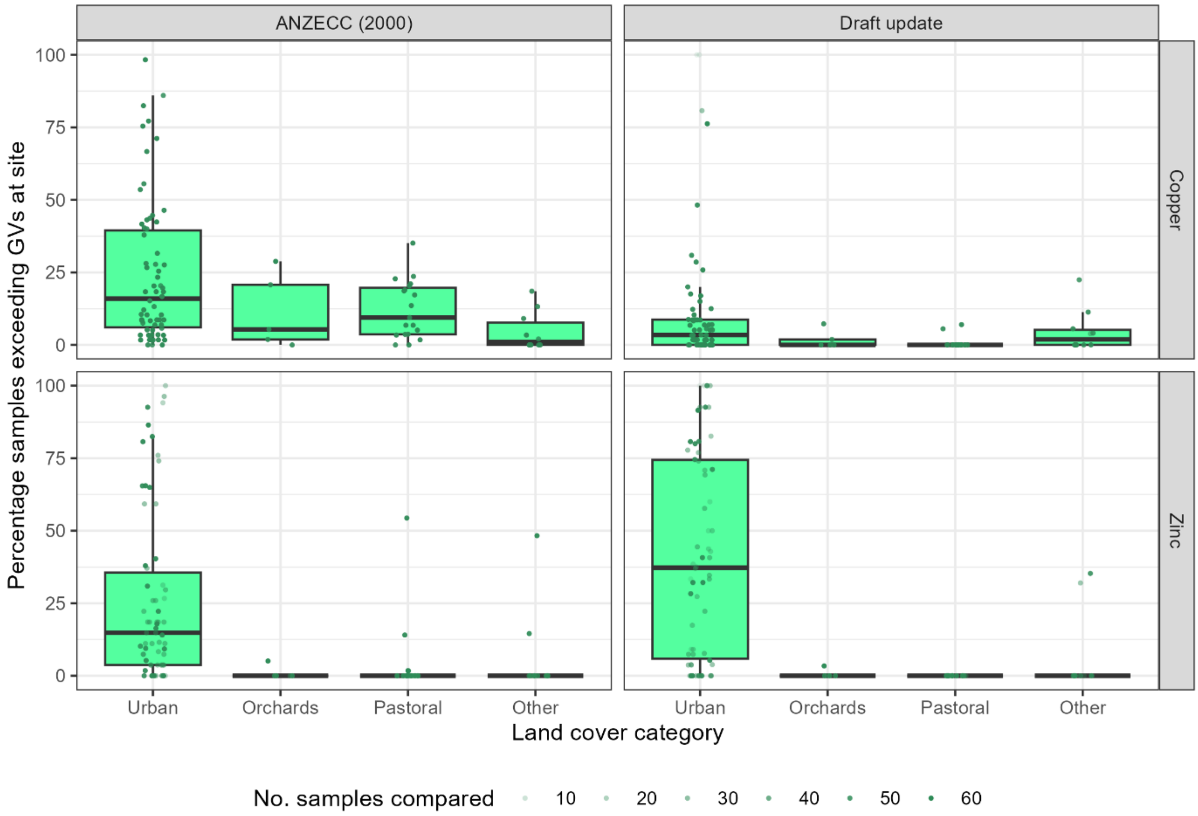


Figure 4-6: Percentage of samples exceeding guideline values at each site, based on comparisons to ANZECC/ARMCANZ (2000) and the draft DGVs. Each site is assigned to a land cover category as described in section 2.4. Each point represents a single site, the colour represents the number of samples that were compared at that site. Box-and-whisker plots show the distributions of these percentages across sites. The black horizontal line in each box indicates the median percentage exceedance, and the box indicates the inter-quartile range (IQR). Whiskers extend from the box to the largest (or smallest) values no more than 1.5*IQR from the box.

ANZG (2018) recommend action if more than 5% of samples at a site exceed the DGV[9]. This percentage is used as a "grading" in Figure 4-7, which shows the number of sites that "fail" (where more than 5% of samples exceed the DGVs) and "pass". Only a small number of sites failed this grading assessment regardless of the DGVs used, and these sites were only those in the urban land cover category.

[9] https://www.waterquality.gov.au/anz-guidelines/monitoring/data-analysis/derivation-assessment

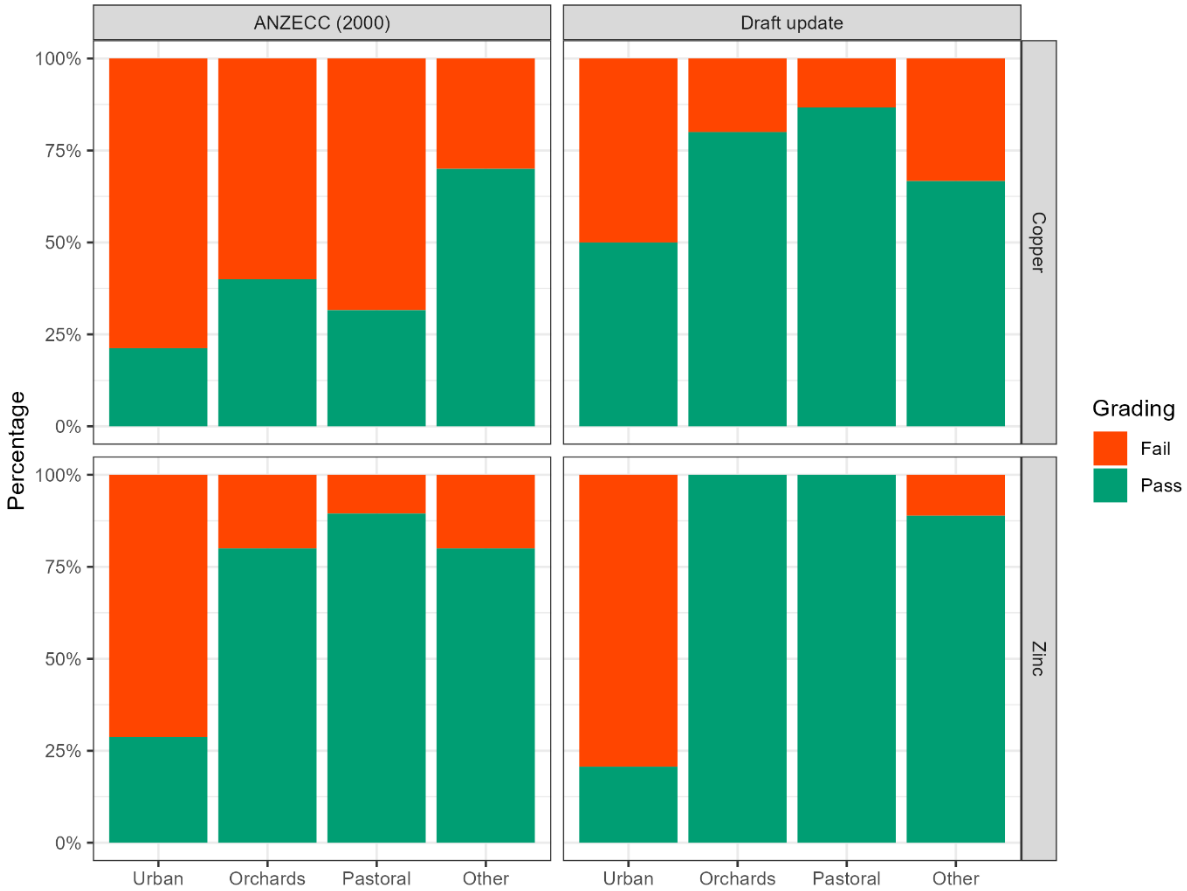


Figure 4-7: Distribution of sites that met the "grading" for dissolved copper and zinc. Each site is assigned to a land cover category as described in section 2.4.

4.4 Relationships between metal state and catchment landcover

The distributions of site-median values of the two dissolved metals are summarized as box-and-whisker plots, with sites grouped by key land cover categories (see section 2.4). There was considerable overlap in the spread of dissolved copper site medians between the land cover categories. Although the median was highest for the orchards category, this is based on only 8 sites, compared to 97 for urban, 36 for pasture and 20 for the other category. For dissolved zinc, the site medians were more often higher at sites in the urban category compared to the orchards or pasture categories.

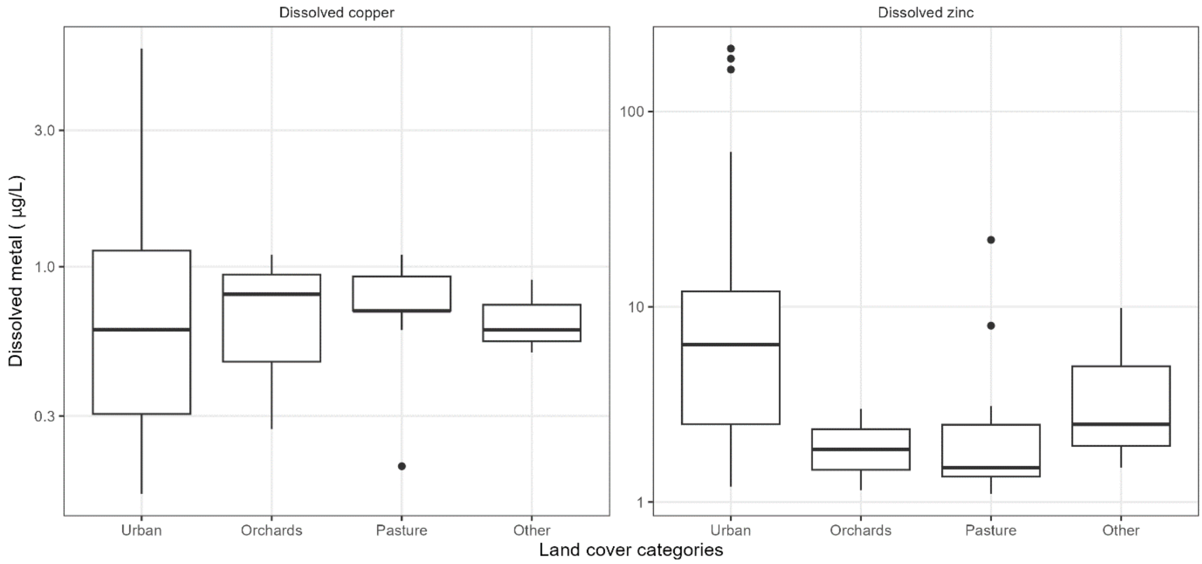


Figure 4-8: Metal concentrations by land cover categories, including the special class of orchards. . Box-and-whisker plots show the distributions of monitoring site medians within land cover categories. Black horizontal line in each box indicates the median of site medians, and the box indicates the inter-quartile range (IQR). Whiskers extend from the box to the largest (or smallest) values no more than 1.5*IQR from the box. Data beyond the whiskers are shown as black circles. Note log-scale on Y-axes.

Scatter plots indicate that dissolved zinc increased with increased urban land cover and impervious surface in the catchment (based on logit transformed data, Figure 4-9 to Figure 4-11). For dissolved zinc, urban land cover, impervious surface and human modified land cover explained 38, 27 and 25% respectively of the variation in the log-transformed dissolved zinc concentration. On the other hand, dissolved copper concentrations could not be explained by the urban land cover, impervious surface area or human modified land cover ($R^2 \leq 0.01$, p-value > 0.05).

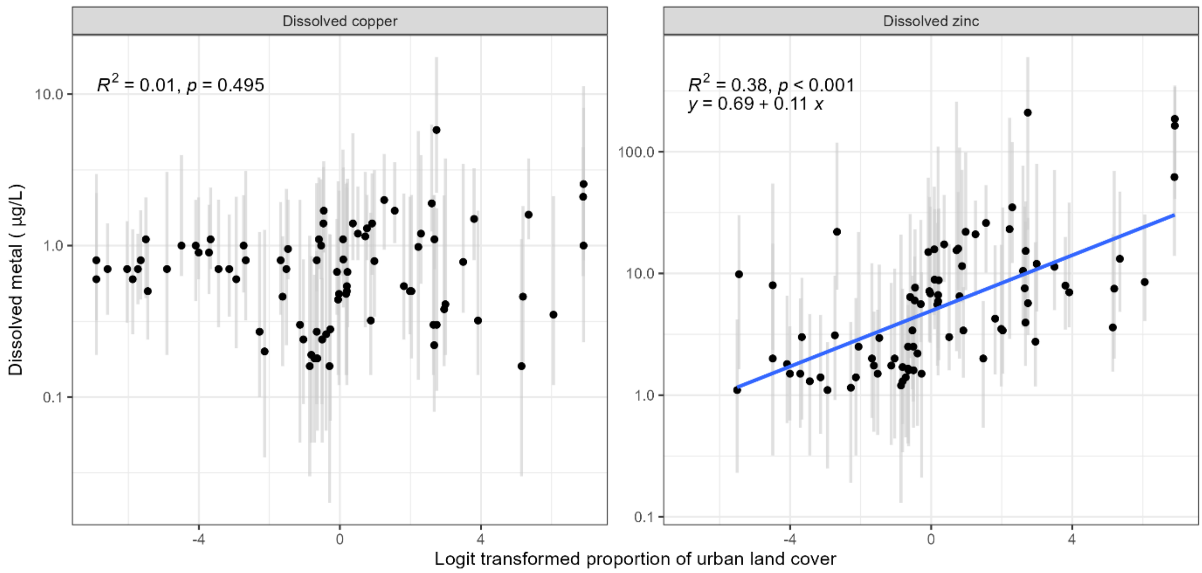


Figure 4-9: Relationships between median water-quality state and logit transformed proportion of urban landcover in the upstream catchments. Solid blue lines indicate least squares linear regression models. Grey lines indicate the range for each site (5th percentile to 95th percentile). Regression equation shown on plot is for log-transformed metal concentration. Analysis excludes sites that did not meet minimum data requirements and where median values were based on imputation.

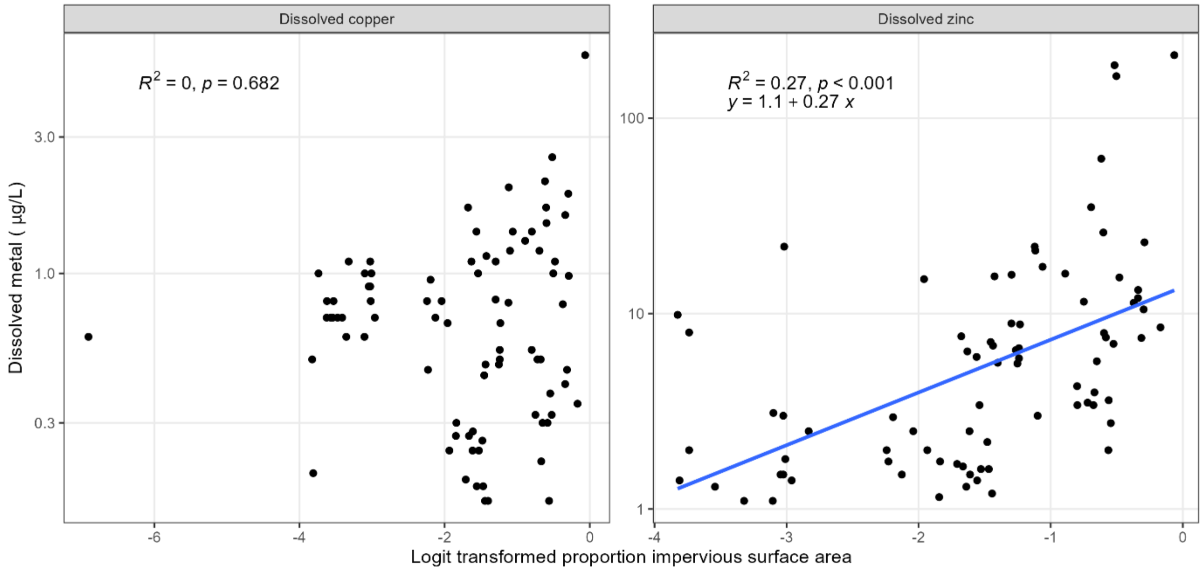


Figure 4-10: Relationships between median water-quality state and logit transformed proportion of impervious surface cover in the upstream catchments. Solid blue lines indicate least squares linear regression models. Regression equation shown on plot is for log-transformed metal concentration. Analysis excludes sites that did not meet minimum data requirements and where median values were based on imputation.

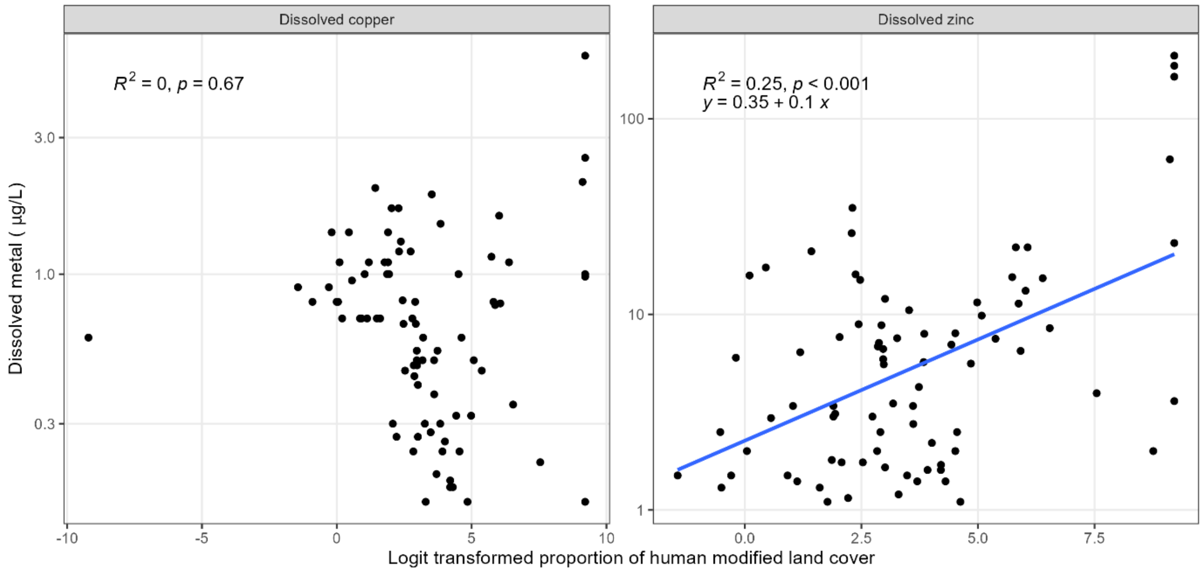


Figure 4-11: Relationships between median water-quality state and logit transformed proportion of human-modified landcover in the upstream catchments. Solid blue lines indicate least squares linear regression models. Regression equation shown on plot is for log-transformed metal concentration. Analysis excludes sites that did not meet minimum data requirements and where median values were based on imputation.

5 Results – river trends

Trends for the ten-year time period and the maximum length that could be assessed are provided in the supplementary files “RawTrendsHiCen10y_230718.csv” and “RawTrendsHiCenLongestPeriod_230718.csv” respectively.

5.1 Ten-year trends (2013-2022)

There were 71 sites that met the filtering rules for assessment of 10-year trends in dissolved copper and dissolved zinc concentrations (Table 5-1). These were located within the Auckland, Wellington and Canterbury regions only (Table 5-1). However, trends for dissolved copper could not be quantified at 21 sites due to the high proportion of censored data. Most of these sites were in Canterbury (19 sites with 97-100% of observations being censored). For dissolved zinc, there were six sites (four in Auckland and two in Wellington) where the proportion of censored data was too high (69-99% of observations being censored) and trends could not be assessed.

Table 5-1: Number of river monitoring sites by region that were included in the 10-year trend analyses of dissolved copper and dissolved zinc.

Region	Number of sites that met filtering rules		Number of sites where trends were assessed	
	Dissolved copper	Dissolved zinc	Dissolved copper	Dissolved zinc
Auckland	23	23	22	19
Waikato	0	0	0	0
Bay of Plenty	0	0	0	0
Wellington	8	8	7	6
Canterbury	40	40	21	40
Otago	0	0	0	0
Total	**71**	**71**	**50**	**65**

5.1.1 Trend direction

For dissolved copper, more sites showed degrading trends in concentrations (that is, increasing concentrations) than improving trends (decreasing concentrations), but for dissolved zinc conversely, more sites showed improving trends than degrading trends (Table 5-1, Figure 5-1).

Table 5-2: Number of sites in each trend category based on assessment of 10 year trends in dissolved copper and dissolved zinc.

Trend category	Dissolved copper	Dissolved zinc
Very likely improving	6	25
Likely improving	9	11
Low confidence in direction	7	12
Likely degrading	8	6
Very likely degrading	20	11

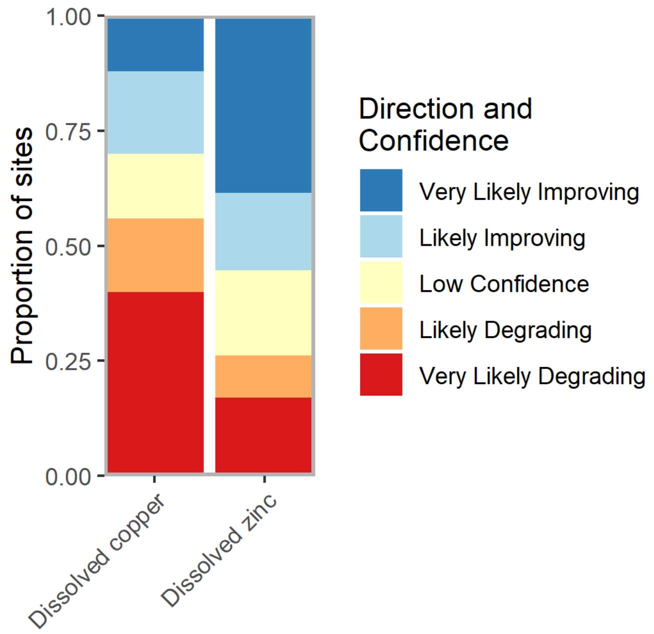


Figure 5-1: Summary plot representing the proportion of river sites with improving 10-year time period trends for dissolved copper and dissolved zinc at each categorical level of confidence and direction. The plot shows the proportion of sites in each of the trend direction and confidence categories defined in Table 3-3.

There were differences in the direction of trends between regions. In the Auckland region, trends in dissolved copper were consistently degrading, whereas in other regions, there was a greater proportion of sites with improving trends in dissolved copper (Figure 5-2 and Figure 5-3). For dissolved zinc, a greater proportion of sites had degrading trends in Canterbury compared to the Auckland and Wellington regions (Figure 5-2 and Figure 5-3).

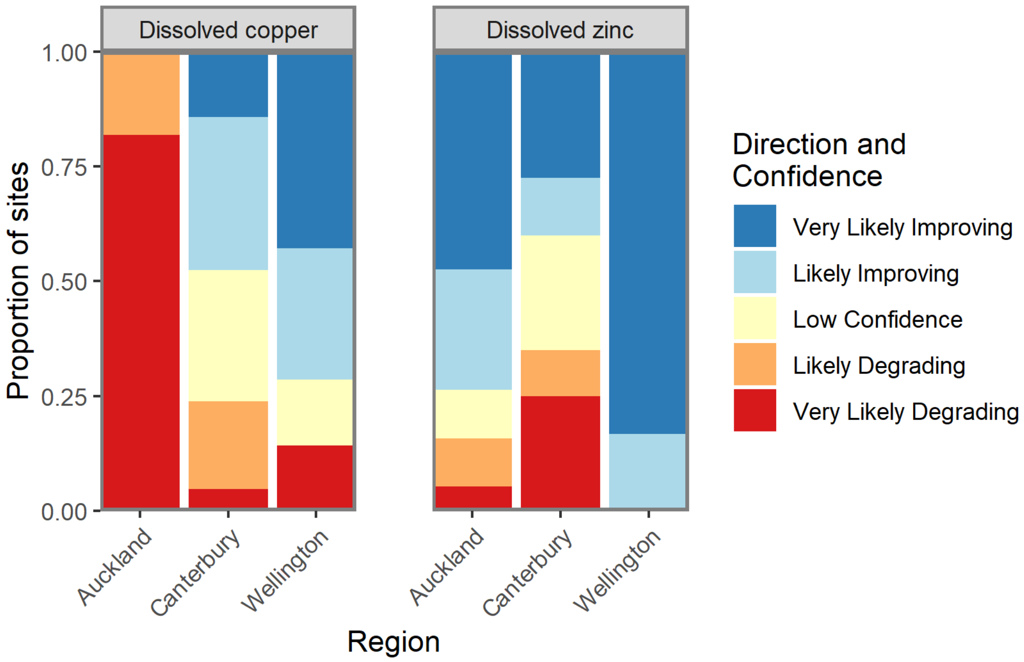
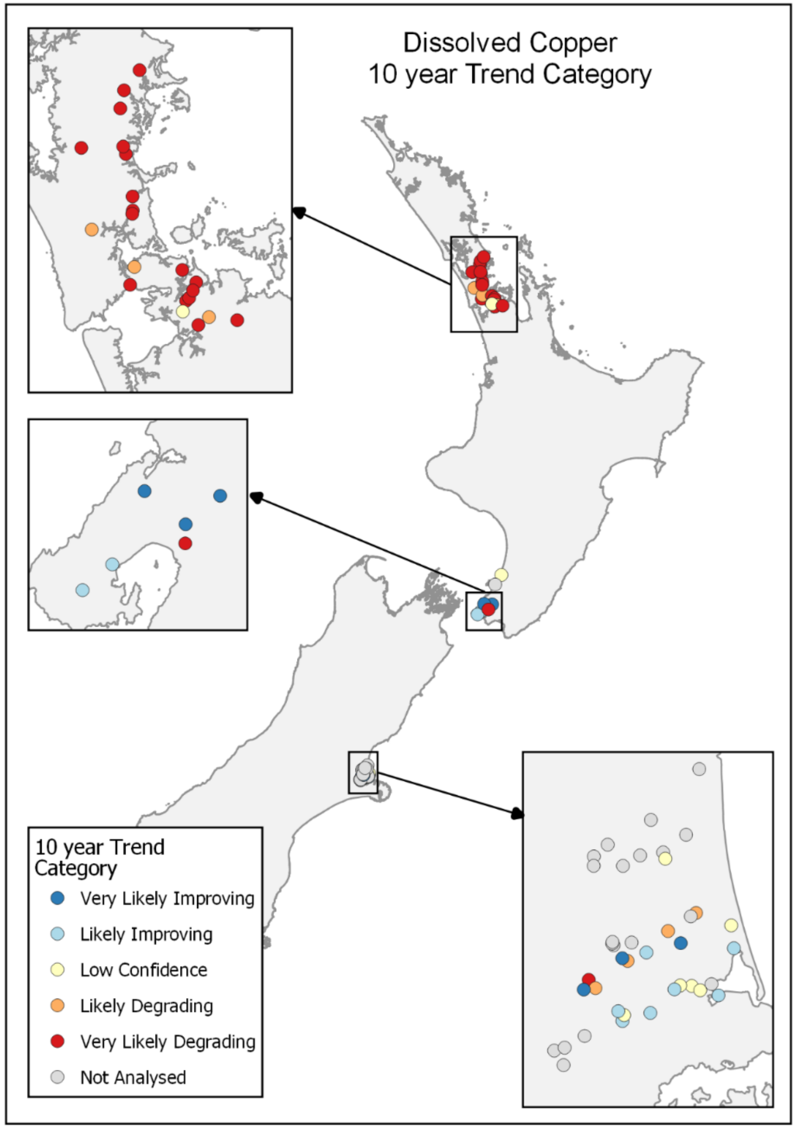


Figure 5-2: Summary plot representing the proportion of river sites, by region, with improving 10-year time period trends at each categorical level of confidence and direction. The plot shows the proportion of sites in each of the trend direction and confidence categories defined in Table 3-3.



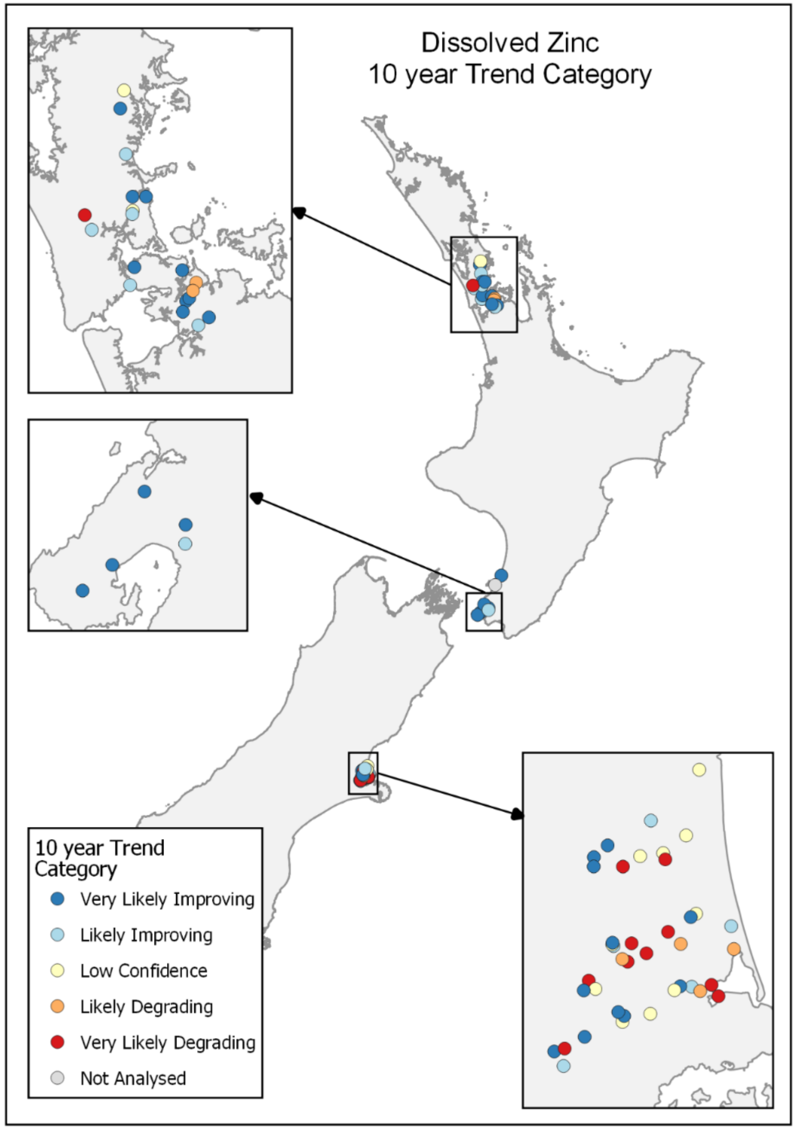


Figure 5-3: Map of river sites classified by 10-year trend confidence and direction for dissolved copper (left) and dissolved zinc (right). Confidence and direction are expressed categorically based on the levels defined in Table 3-3.

5.1.2 Trend rate

Trends rates for dissolved copper and dissolved zinc are plotted against the proportion of upstream urban land cover (Figure 5-4) and impervious surface area (Figure 5-5). All estimated trend rates are included in these plots, irrespective of the level of confidence in the assessment, excluding sites where trends could not be assessed due to high levels of censoring. These plots do not indicate any systematic relationship between these catchment characteristics and trend rates. For example, both increasing and decreasing zinc concentrations were observed at sites with high percentages of urban land cover.

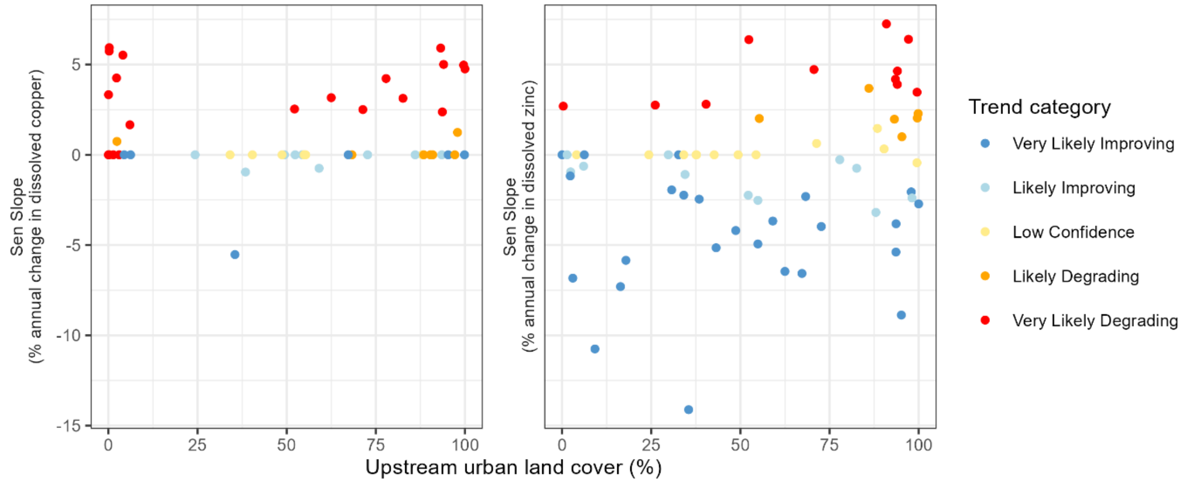


Figure 5-4: 10-year trend rates (annual change) versus the proportion of urban land cover in the upstream catchment. Colour of point indicates confidence and direction expressed categorically based on the levels defined in Table 3-3.

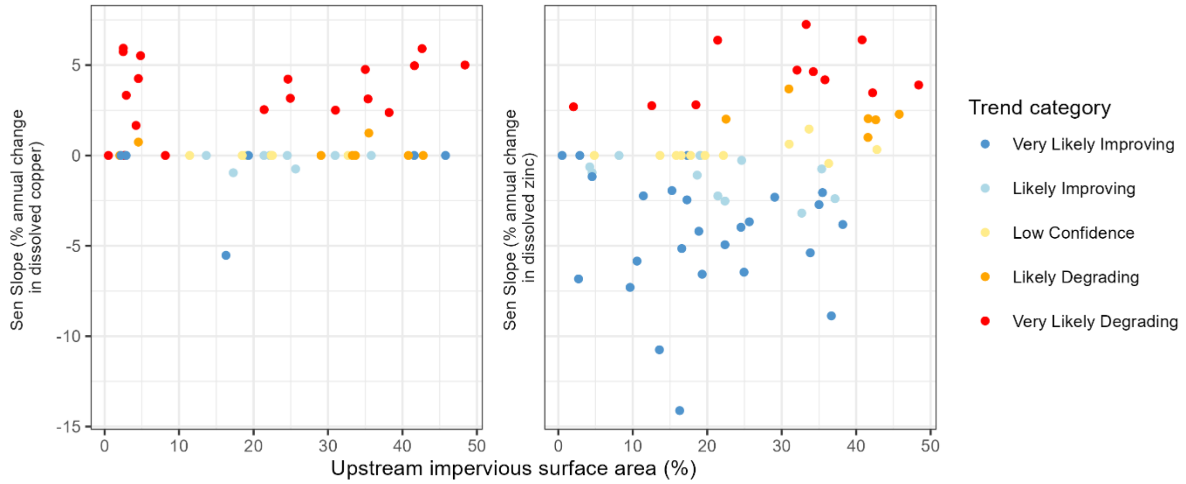


Figure 5-5: 10-year trend rates (annual change) versus the proportion of impervious surface area in the upstream catchment. Colour of point indicates confidence and direction expressed categorically based on the levels defined in Table 3-3.

5.2 Variable length trends (2006-2022)

Although there were 114 sites that met the filtering rules for assessment of trends based on any length (Table 5-3), trends could not be quantified for 10 of those sites for dissolved copper and 11 sites for dissolved zinc due to the high proportion of censored data. These sites were in the Auckland, Wellington, Canterbury and Otago regions.

Trends in dissolved copper and dissolved zinc concentrations could be quantified at five and six sites respectively in the Otago region, but only over a four-year period (Figure 5-6). Similarly, there were around 12-13 additional sites in Auckland and 27-28 additional sites in Canterbury where trends could be quantified over a period of three to six years (Table 5-3, Figure 5-6). For Canterbury, this was due use of a lower detection limit for dissolved copper from October 2016, which meant fewer data were censored from that period onwards.

The longest period used for trend assessment was 17 years, for eight sites in the Auckland region (trend period from January 2006 to December 2022). Although both dissolved copper and zinc were routinely monitored before 2006 at these sites, the dissolved copper and zinc detection limits prior to May 2005 were 10x and 5x higher, respectively, than the detection limits used from 2006 to 2022. Consequently, for some of the sites most of the pre-2006 data were censored. For sites with lower proportions of censoring, the hi-censor method (to account for the changes in detection limits) would have obscured trends during the assessment period. For these reasons, the trends were assessed for a period that started after the reduction in detection limits.

Table 5-3: Number of river monitoring sites by region that were included in the trend analyses of dissolved copper and dissolved zinc based on the longest period that could be assessed*.

Region	Number of sites that met filtering rules		Number of sites where trends were assessed	
	Dissolved copper	Dissolved zinc	Dissolved copper	Dissolved zinc
Auckland	36	35	32	26
Waikato	0	0	0	0
Bay of Plenty	0	0	0	0
Wellington	10	10	9	9
Canterbury	62	63	58	62
Otago	6	6	5	6
Total	**114**	**114**	**104**	**103**

Note: * Length of trend period ranged from 3 to 17 years.

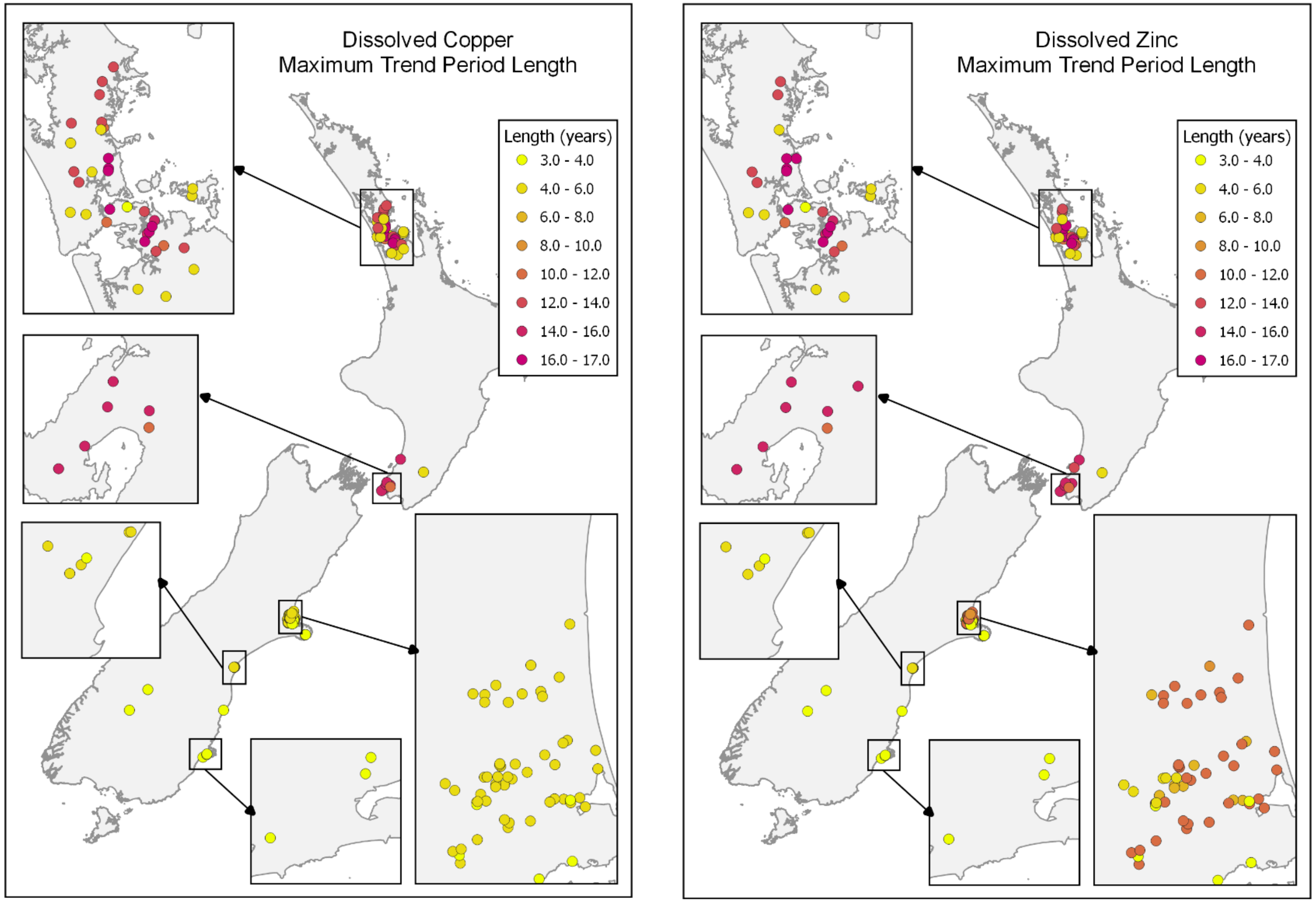


Figure 5-6: Maps of monitoring sites coloured by their maximum trend period length, for dissolved copper (left) and dissolved zinc (right)

5.2.1 Variable-length trend direction and rate

For both dissolved copper and dissolved zinc, more sites had improving trends in concentrations (that is, decreasing concentrations) than degrading trends (Table 5-4). For dissolved copper, this is in contrast to the 10-year trends (Table 5-2) and is mostly due to the inclusion of the additional Canterbury sites, where there were either likely or very likely improving trends at 45 sites, based on the most recent six-year period (Figure 5-7).

Trend confidence should not be compared between sites as the trend period varied from 4 to 17 years, and confidence in trend direction is strongly influenced by the number of samples.

Table 5-4: Number of sites in each trend category based on assessment of variable length trends in dissolved copper and dissolved zinc.

Trend direction	Dissolved copper	Dissolved zinc
Increasing	39	37
Decreasing	65	66

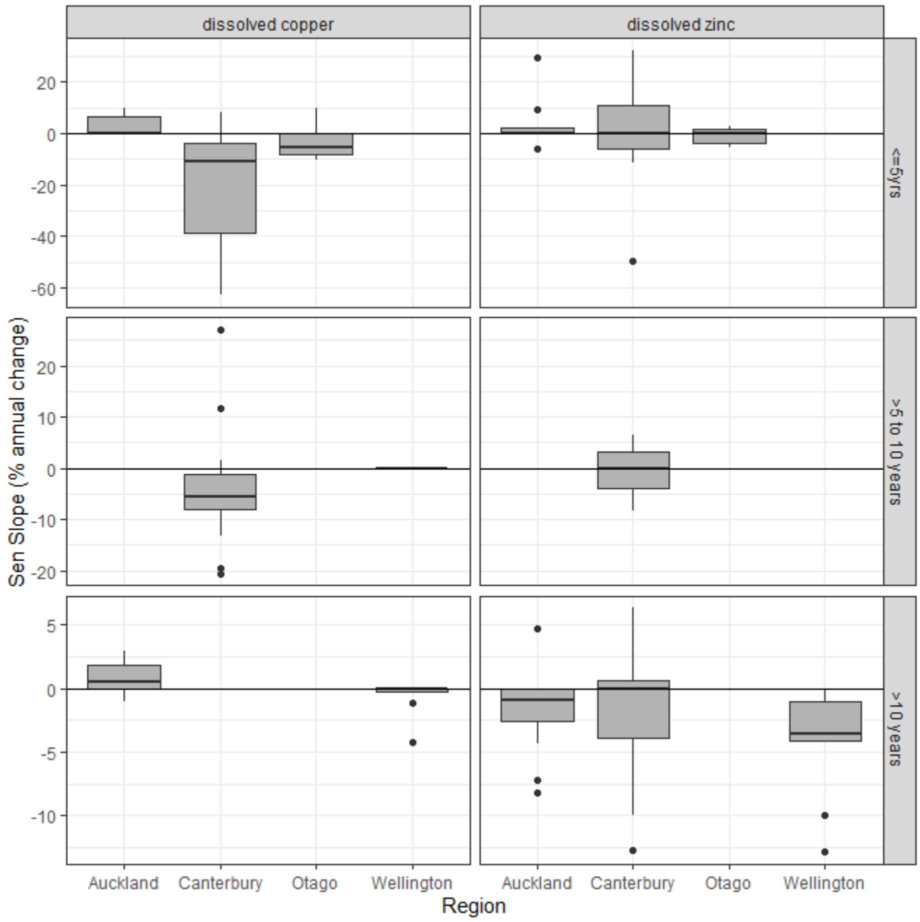


Figure 5-7: Rate of change in dissolved copper and dissolved zinc based on region and trend period assessed.

6 Discussion

The primary purposes of the state and trend analyses reported here are to provide MfE with information required for reporting on the freshwater domain. The detailed information for each river monitoring site is contained in the supplementary files that accompany this report. The sites and their water quality assessments (i.e., state and trends) can be aggregated in many ways to meet different information requirements (e.g., grouped by region or environmental class, distributed along environmental gradients.).

In this report we limited our summaries of the results to example tables and plots, and we focus this discussion on the methods used and limitations of the assessment, rather than a detailed interpretation of the results.

6.1 State

6.1.1 Changes to state assessment methods

We have generally used the same state assessment methodology as used in the previous national-scale water quality state analyses (Larned et al. 2018) and the previous analyses of dissolved copper and dissolved zinc (Gadd et al. 2019), with some minor differences:

1. we used a five-year period for assessing state (differing from the previous assessments of metals, but consistent with national river water quality assessments).

2. we excluded data that were identified by data suppliers as low quality (NEMS categories QC400 or equivalent),

3. the minimum data requirements were more lenient than in previous assessments, requiring data for 80% of the years and 80% of the seasons. This compares to the earlier studies requiring 90%. The change was to account for the slightly lower number of observations at each site after low quality data were excluded. The 80% threshold is consistent with that used for the assessment of lake water quality (Whitehead et al. 2021), and

4. Dissolved copper and zinc concentrations were compared to draft updated default guideline values (DGVs) that for dissolved copper require adjustment based on concentrations of DOC and for dissolved zinc, based on concentrations of DOC, hardness and pH. As these variables were not measured at all sites in all samples, only a subset of the data could be compared to these DGVs.

6.1.2 Discussion of state results

This assessment included a larger data set compared to previous assessments: extending beyond urban streams and including data from the Waikato, Bay of Plenty and Otago regions. Only data from Auckland, Wellington, Canterbury and Otago regions met the filtering rules; however data from Waikato and Bay of Plenty indicated that copper and/or zinc concentrations in those regions are similar to those found elsewhere in New Zealand. There were no obvious differences in the metal concentrations between regions but both metals were positively associated with urban land cover and impervious surface area in the catchment.

6.2 Trends

6.2.1 Changes to trend assessment methods

The methods used to assess trends in this report differ somewhat from those previously used to assess trends in dissolved copper and zinc (Gadd 2016, Gadd et al. 2019). These changes have largely been made to align the reporting with recently published trend guidance (Helsel et al. 2020; Snelder et al. 2021). The main difference between this assessment and the previous assessments is in the use of a method to account for the multiple detection limits that were used the analysis of many of the water samples (see 3.2.2 for details).

Table 6-1: Summary of differences in trend assessments between reports..

	Gadd (2016)	Gadd et al. (2019)	This report
Number of years assessed	8 years	10 years	10 years
Data time frame	Jan 2008 to Dec 2015	Jan 2008 to Dec 2017	Jan 2013 to Dec 2022
Censoring limits	<15% censored data	No limit*	No limit*
Handling censored data	Imputation	Censored values included	Censored values included with consistent (highest) detection limit applied through the assessment period
Method to assess trend direction	Mann Kendall, using imputed values for censored data	Mann Kendall, using pairs to assess censored data	Mann Kendall, using pairs to assess censored data
Method to assess trend rate	Seasonal Sen Slope Estimator	Seasonal Sen Slope Estimator	Seasonal Sen Slope Estimator
Trend confidence and direction categories	Increasing, decreasing, indeterminate	9 levels based on Stocker et al. (2014).	5 levels

Note: * Although no specific limit was applied, the trend cannot be calculated if there are < 5 non-censored values and/or <3 unique non-censored data.

6.2.2 Discussion of trend results

Although copper and zinc are both common contaminants in urban stormwater, there were differences between dissolved copper and dissolved zinc in the predominant directions of 10-year trends. There were more sites with degrading trends for dissolved copper, whereas for dissolved zinc, more sites showed improving trends.

This may be related to changes in the specific sources of each metal – for example, increases in copper may be related to increases in traffic or traffic congestion, as brake pads are a key source of copper. Decreases in zinc may be related to reduced use of unpainted zinc-based roofing.

The predominately degrading trends in dissolved copper are largely due to the consistent degrading trends in the Auckland region, where degrading trends were assessed at all of the 22 sites (out of a total of 50 sites assessed in New Zealand). In Canterbury and Wellington trend directions were improving and degrading. Only 5 out of 21 sites in Canterbury and 1 out of 7 sites in Wellington had degrading trends in dissolved copper. In Auckland there was a change of laboratory midway through the ten-year period (July 2017). The change in detection limit was accounted for in the trends assessment as the detection limit was higher from July 2017 to December 2022 than the preceding period. However, accounting for changes in the detection limit does not account for other differences that may occur due to changes in laboratories (e.g., subtle changes in filtration methods or storage times that result in changes in the metal concentrations measured).

6.3 Limitations of this assessment

Trends in water quality are known to be influenced by climatic variability (Scarsbrook et al. 2003, Snelder et al. 2022b). The national river water quality trend analysis included an assessment of rolling trends (using different ten-year windows to assess trends) and shows that the trend rate and direction fluctuate over time (Whitehead et al. 2022b). This report did not include any assessment of rolling trends - this could only be undertaken for approximately 4-7 "windows" based on the duration of metal monitoring, and only at sites located in Auckland (20 sites) and Wellington (8 sites). When a longer period of record is available for more sites, it would be useful to assess rolling trends for dissolved copper and zinc, and to assess if changes in the trend direction can be attributed to climate variability.

There are some limitations in the comparison of dissolved copper and zinc median concentrations to catchment land cover and impervious surface area. Firstly, the digital river network was used to identify the upstream catchments based on the stream segment on which the sampling site was located. In some cases, sampling sites are located as the upper end of a stream reach, and the associated catchment therefore does not drain to the sampling site, and characteristics of that catchment would not influence the water quality at that site. This is also the case in the national assessment of river water quality state, however in this current assessment, most sites are lower order streams (first and second order) with small catchments (meaning that these errors have more significance). Furthermore, many of the sites are located at the fringe of an urban area meaning there is potentially greater variation between upstream and downstream land covers. With fewer sites included in the state assessment for metals (100 compared to over 800 in the assessment for other water quality variables), these minor issues may have greater effect on the relationships assessed by this study.

The impervious surface area was estimated based on building footprints and roading polygons. While this is an adequate representation of impervious surface in many locations, especially at a broader level, there may be sites with much higher impervious surface area than calculated, due to the presence of other paved surfaces (such as driveways, carparks and industrial yards). This adds some additional uncertainty to the relationships between metal concentrations and impervious surface area.

7 Acknowledgements

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Appendix A Summary of metal monitoring undertaken in NZ

Council	Abbrev.	Monitoring undertaken	Sites	Dates
Northland Regional Council	NRC	Total copper and zinc	16 sites	March 2023
Auckland Council	AC	Dissolved copper, zinc	~40 sites, varying over time	Various start dates – ongoing
Waikato Regional Council	WRC	Total and dissolved Cu, Zn	6	Quarterly 1995-1997
			82	Monthly Aug 2009 - Jul 2010
			16	Monthly Mar 2018-Feb 2019
Environment Bay of Plenty Regional Council	EBOP	Dissolved copper, zinc	5 sites	Sporadically since 2019
Gisborne District Council	GDC	Nothing received		
Hawkes Bay Regional Council	HBRC	Dissolved copper, zinc	5 sites	Approx quarterly monitoring 2007 -2013
Taranaki Regional Council	TRC	Nothing received		
Greater Wellington Regional Council	GWRC	Dissolved copper, zinc	11 sites, increasing to 17 sites in 2020	Monthly monitoring since Jan 2008
Nelson City Council	NCC	Nothing received		
Christchurch City Council	CCC	Dissolved Cu, Zn	> 30, varying over time	Monthly since Feb 2011
Environment Canterbury	ECan	Dissolved Cu, Zn	~ 30	Quarterly and/or for investigations only
Otago Regional Council	ORC	Dissolved Cu, Zn	6	Monthly since Jul 2018
Environment Southland	ES	Not currently monitored		