Metal Partitioning

Investigations to improve modelling by the Freshwater Management Tool

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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.

This work was commissioned to investigate the partitioning of zinc and copper in Auckland streams and stormwater to support the representation of these metals in the FWMT. The objectives of this study were to:

1. Characterise and compare the partitioning of zinc and copper in Auckland's rural and urban streams and stormwater into particulate and dissolved fractions.
2. Investigate the factors that could be causing the differences in partitioning between rural and urban streams and stormwater.
3. Compare observed partitioning against the partitioning factors used in the FWMT.
4. Make recommendations on metal monitoring and representation of zinc and copper partitioning in the FWMT.

Observed stream water quality came from Auckland Council's State of the Environment (SoE) reporting (34 sites, data periods varying between 3 and 17 years), and data on stormwater quality primarily came from NIWA's Urban Runoff Quality Information System (URQIS) database supplemented with additional published and unpublished stormwater data. The data were analysed using exploratory data analysis and statistical learning techniques to investigate factors associated with the partitioning.

The FWMT simulates the concentration of total zinc and total copper in streams. These simulated concentrations are multiplied by a universal partitioning parameter (0.676 for copper and 0.688 for zinc), called the metal ratio in this report, to calculate the dissolved concentrations of metals in FWMT modelled streams. The average observed ratios of dissolved to total metals in Auckland streams as determined in this study were similar to those used in the FWMT (i.e., the additional sites and records since 2017 did not alter the regional median metal ratios substantially)..

There was a tendency for non-urban streams to have the highest metal ratios (meaning more metals in dissolved form). For copper, the median ratios were 0.766, 0.690 and 0.408 for non-urban and urban streams and stormwater. The corresponding ratios were 0.727, 0.667, 0.631 for zinc. However, the range of ratios between the source types overlapped and there was considerable variation in partitioning within individual monitoring sites.

The key factors that explain the variation in metal ratios were the concentration of total suspended solids (TSS) and the concentrations of other metals. Higher concentrations of total metals and TSS tend to result in lower copper and zinc ratios (less metal in dissolved form). Other factors that were found to be related to metal ratios were time (on a seasonal timescale), pH and dissolved organic carbon, flow and land use. Some of these are correlated, for example higher flows are associated with higher particulate matter concentrations in water (TSS). These factors could not explain all the observed variation in the data. There was considerable "noise" in the data, perhaps partly because the metal concentrations in streams, particularly non-urban streams, tend to be low and close to the detection limit.

Recommendations were made, including:

1. Consideration should be given to using variable metal partitioning parameters within the FWMT to estimate dissolved metals, using the models developed in this project.

2. Laboratory methods to measure metals with lower detection limits than those currently used by the Council should be considered.

3. High-frequency monitoring of water quality parameters, including metal concentrations and TSS and flow during high flow events, will provide more insight into the dynamics of metals and their partitioning than the current SoE monthly sampling approach.

1 Introduction

Auckland Council (AC) is responsible for freshwater quality regulation and management across the Auckland region, including implementation of the National Policy Statement for Freshwater Management (NPS-FM - (New Zealand Government 2020)). The Freshwater Management Tool (FWMT) programme is led by Healthy Waters to provide AC with essential decision making support for the NPS-FM (Healthy Waters 2020).

The FWMT programme includes development of a continuous, process-based water quality model that covers all the Auckland region's freshwater catchments, from headwaters to coast inclusive of all rural and urban areas. The FWMT model ("FWMT") simulates processes that generate, transport, and affect the fate of contaminants (sediment, nutrients, metals and faecal indicator bacteria) from land to water using US EPA base models ((Healthy Waters 2020). This includes the simulation of sediment, total copper and zinc within in streams on a continuous (15-minute) basis. The FWMT simulates copper and zinc in total forms only with post-processing to estimate dissolved metal concentrations.

It is important to estimate the dissolved forms, as these are the most important forms in predicting risks for freshwater ecosystems (Prothro 1993). For the FWMT, the in-stream concentration of dissolved copper and zinc are currently estimated by multiplying the simulated total metal concentration by a partitioning parameter (0.676 for copper and 0.688 for zinc), called the "metal ratio" in this report. These metal ratios were derived after examination of metal ratios from Auckland Council State of Environment (SoE) monitoring data. Despite wide variation, there was no distinct spatial (watershed) variation and a regionwide median of the metal ratios from SoE observations was adopted (that is, a universal ratio across space, time and flow). A subsequent review of the FWMT highlighted that the simplifying modelling assumption of fixed partitioning should be investigated further (Hamilton et al. 2021).

This work aims to elucidate factors that influence metal partitioning. In addition, Understanding partitioning will help Auckland Council in three ways. Firstly, the improved knowledge could be incorporated into future developments of the FWMT. Secondly, this knowledge could help in targeting monitoring to improve the FWMT and other initiatives. Thirdly, it will help stakeholders understand the uncertainties in the current model. The primary objectives of this project are to provide information for the first and second of these. Specifically, the objectives are to:

1. Characterise and compare the partitioning of zinc and copper in Auckland's rural and urban streams and stormwater into particulate and dissolved fractions.
2. Investigate the factors that could be causing the spatial and temporal differences in copper and zinc partitioning.
3. Compare observed partitioning against the partitioning used in the FWMT.
4. Make recommendations on metal monitoring and representation of zinc and copper partitioning in the FWMT.

This work takes an observational study approach and is informed by peer-reviewed literature.

The observational study analysed approximately 20 years of State of the Environment (SoE) monitoring data from rivers across the Auckland region. This data was supplemented by information on stormwater quality taken from NIWAs Urban Runoff Quality Information System (URQIS).

Stormwater is a significant contributor to heavy metal contamination in urban streams (Ingvertsen et al. 2011), particularly in Auckland (Abar et al. 2017, Mills & Williamson 2008). Gadd et al. (2020) noted that dissolved zinc concentration was positively correlated with the proportion of urban land cover but did not consider how metals were partitioned.

Overseas work has identified several factors associated with the partitioning of metals in streams and the processes involved. Total metals are associated with particulate matter; the higher the total suspended solids (TSS) levels, the higher the total metals levels (Andarani et al. 2021, Baum et al. 2021, El Azzi et al. 2013, Zhang et al. 2022). Flow, which is also related to TSS concentrations, pH and Dissolved Organic Carbon (DOC) are all factors associated with the level of metals (Heier et al. 2010, Lu & Allen 2001). These studies found that the partitioning of metals between particulate and dissolved states is also associated with TSS, flow, DOC, pH and total metals, as well as preceding hydrological conditions. It should be noted that when particulate metals are discussed, it generally means "sorbed" metals, in other words, metals are attached to particles rather than the metals being bound within minerals making up the particles. Sorbed metals are generally less bioavailable than dissolved metals, but they can become desorbed (Miranda et al. 2021, Miranda et al. 2022). The partitioning depends on water chemistry and the surface properties of particles (Lu & Allen 2006). Prestes et al. (2006) and Lu and Allen (2006) both identified that the proportion of the sorbed metal (particulate metal concentration) relative to dissolved metal decreased with increasing TSS. The amount of adsorption depends on particle sizes, with higher metal particulate concentrations on finer particles (Baum et al. 2021). Though heavy metals such as copper and zinc display similarities in their behaviour, their behaviours are not the same, so both need to be investigated.

1.1 Layout of this report

This report follows the structure of methods, results and discussion and implications for the FWMT in the sections as outlined below.

- The method section (Section 2) briefly describes the observational data used and data analyses undertaken.
- The results and discussion section (Section 3) presents the analysis of data. It provides an interpretation of these findings in light of our knowledge of stormwater and stream water processes.
- The implications section (Section 4) pulls the information together in the context of the FWMT. It makes recommendations as to how the results of this report can be used to inform future iterations of the FWMT.

2 Methods

This project identifies patterns and factors associated with the partitioning of copper and zinc in stream water and stormwater. It takes an observational study approach, using Exploratory Data Analysis (EDA) and statistical modelling, to identify these patterns and factors. The project made use of pre-existing datasets. In this section, we discuss:

- How partitioning is defined,
- Data and data quality
- Statistical analysis

Readers, who are short on time, may wish to skip this section and move straight to Results and Discussion. However, this section does provide details of the approach used.

2.1 Definition of metal partitioning

Copper and zinc can occur in either dissolved or particulate forms. The dissolved (or soluble) form is typically defined as the fraction that passes through a filter with 0.45 µm pores. This definition is consistent with the Auckland Council's SoE monitoring and the stormwater studies included in the URQIS data[1]. "Total metals" is a measure of the total amount of copper or zinc present in a sample, as measured after digestion with acid[2], and therefore includes both those dissolved and those attached to suspended particles (particulate forms). The dissolved form is the form most relevant for assessing potential toxicity, as it is this form that is most bioavailable to aquatic organisms and therefore typically used in comparison to water quality guidelines (USEPA 1996, Warne et al. 2018).

The partitioning parameter used in the FWMT is called the metal ratio, in other studies, it is often referred to as the partitioning index (Baum et al. 2021). The metal ratio is the ratio of dissolved to the total metal as defined below for copper and zinc (1,2). A value of one implies that all the metal is in a dissolved (soluble) form, and zero implies that all the metal is in an insoluble (particulate) form.

$$Copper\ ratio = \frac{Dissolved\ copper}{Total\ copper} \tag{1}$$

$$Zinc\ ratio = \frac{Dissolved\ zinc}{Total\ zinc} \tag{2}$$

2.2 Data and dataset

2.2.1 Data sources

This study used two pre-existing water quality datasets: Auckland SoE monitoring of rivers and streams around the region and the URQIS database for stormwater (within the piped network) monitoring. The key water quality attributes extracted from these two data sets were total and dissolved zinc and copper, total suspended solids (TSS), and metadata such as the upstream land use/land cover.

[1] Some other definitions refer to filters with different pore sizes, e.g., 0.2 µm or 0.4 µm.

[2] Note that most monitoring studies measure "total recoverable" metals which uses acid digestion to extract metals weakly or strongly bound to particulate material, but does not usually extract metals from within minerals.

Auckland Council's SoE water quality monitoring began in 2003 with monthly water quality samples collected from 34-37 sites (the number of sites has changed slightly over time; see Ingley and Groom (2021)). In addition to metals and TSS, soluble calcium, soluble magnesium, total alkalinity, total hardness, total suspended solids (TSS), dissolved non-purgeable organic carbon (DNPOC), electrical conductivity (lab and field), pH (lab and field), and water temperature were extracted from the data set. Metals were initially monitored at only 4 sites, increasing to a total of 23 by 2012, with a further 11 sites added in June 2018 (see Appendix A) [3]. Data for the water quality attributes were obtained from their first collection date until June 2021, which therefore varied from a 17-year period (221 observations) to approximately 3-years (36-39 observations). In addition, calcium, magnesium, alkalinity and DNPOC were only available from November 2017.

Streamflow is measured continuously at or hydrologically close to 16 of the water quality monitoring sites in the dataset. Monitoring of flow and water quality only coincided at 14 sites. As flow varies considerably between sites, two approaches were used to allow comparability during analysis: the first approach grouped data into categories based on flow, and the second scaled flow from zero to one. In the first approach, the category of "High" is used for stream flows of the highest 10% of the observed flow in that stream, and "Low" when the flow was in the lowest 50% (i.e., below median flow). The latter approximately equates to low flow conditions. Data in the third category (neither "High" nor "Low" were excluded. This approach was adopted to isolate model performance during high and low flows in the Freshwater Management Tool: Baseline Configuration & Performance Report (see p 171, Auckland Council 2020). The second approach normalised flows by scaling them on a scale from zero to one (Patro & Sahu 2015) to allow comparability between streams. The value zero is the minimum, and one is the maximum observed flow at that site.

As well as information about the quantity and quality of water in the stream, Auckland Council provided information associated with various land uses in the area upstream from the monitoring sites (FWMT v1.0 hydrological response unit information on land cover and impact classes). Plus, each site was classified into one of four classifications based on surrounding land use: Reference, Exotic Forest, Rural & Lifestyle (includes all non-forested rural land, pastoral and horticultural uses) and Urban using the scheme described by Buckthought et al. (2020), except Redwood Stream, which was reclassified as Exotic Forest based on discussions with Auckland Council (R. Ingley, pers.comm.) and consistent with Ingley and Groom (2022).

Stormwater data came from the Urban Runoff Quality Information System (URQIS) database (urqis.niwa.co.nz) developed by NIWA and partially funded by Auckland Council. URQIS is a resource that provides stormwater and urban stream water quality data from all over New Zealand compiled by NIWA (Gadd et al. 2014, Gadd et al. 2013). These data are from a range of different studies, typically one-off investigations, including single discrete samples collected at a site, to samples collected throughout multiple rainfall events. Only data from untreated stormwater were included in the data set used. The oldest data included in that dataset were collected in 2001, from extensive studies conducted in Auckland City and the newest data were from 2012. Sormwater data from URQIS were supplemented by data from additional studies, which will be entered into URQIS in due course. These studies include roof runoff from Auckland (Kingett Mitchell Limited and Diffuse Sources Limited 2003, Pennington & Webster-Brown 2008), stormwater from three Auckland sites (two commercial, one carpark, NIWA unpublished data); and data from Christchurch (road, carpark and roofing) (Charters et al. 2017, Charters et al. 2021, Poudyal et al. 2021, Wicke et al. 2009). The overall stormwater dataset is therefore made up of multiple independent studies that included total

[3] One site has no metal data associated with it

and dissolved forms of copper and zinc and TSS, as well as metadata such as land use. All data included were discrete samples (i.e., not event-mean concentrations).. Land use was a generic term used in this study to describe both land covers (such as roads and roofs) and land uses (such as urban, residential or industrial areas).

2.2.2 Data quality

A basic check on data quality was carried out before the data analysis to ensure values were in the correct format, and there were no apparent errors, such as figures being the incorrect orders of magnitude.

We analysed only SoE data that have been quality assured by Auckland Council in keeping with the Auckland Council Research and Evaluation Unit (RIMU) general approach. The URQIS data had also been quality assured by NIWA. This means we are confident that the data accurately reflects the composition of stormwater and stream water.

This work had to manage two significant data quality challenges: missing data and censored data. Missing data is when one or more measured attributes are not present in the dataset. Censoring is when the attribute is present, but the measured value is below the laboratory limit of detection (LoD).

There are three common ways to deal with missing data: imputation (Nijman et al. 2022), listwise deletion, and pairwise deletion (IBM 2020). Imputation involves replacing missing data with an educated guess. Listwise deletion means removing an observation from the whole analysis, where an observation is a sample taken at a point in time and all its associated attributes. This work uses the third-way, pairwise deletion. Pairwise deletion involves using observations with missing data providing the analysis does not call for the attribute(s) that is missing. If the attribute is missing, then that observation is excluded from the analysis in question but not the whole analysis. Pairwise deletion is a more efficient use of the data than listwise deletion, but it does mean that the number of observations used can vary from analysis to analysis of the same dataset.

Censored data refers to values below a laboratory method's limit of detection (LOD). Approximately 8% of total copper and 17% of dissolved zinc values were censored in the SoE dataset. Prior to 2006 the reported LOD values were 0.005 mg/L for dissolved copper, 0.006 mg/L for total copper, 0.06 mg/L for dissolved zinc and 0.06 mg/L for total zinc. Between 2006 and 2016 these levels fell to between 0.00001 and 0.0005 mg/L for for dissolved copper, 0.0001 and 0.0005 mg/L for total copper, 0.0005 and 0.0003 mg/L for dissolved zinc and 0.0003 mg/L for total zinc. From 2017 onward the reported LOD values rose to 0.0005 mg/L for dissolved copper, 0.00053 mg/L for total copper, 0.0003 and 0.0010 mg/L for dissolved zinc and 0.0011 mg/L for total zinc. Approximately 18% of the SoE observations were censored for zinc and or copper, in contrast only 0.2% of the stormwater samples were censored. This reflects the fact that stormwater samples had higher metal concentrations than the river samples collected by SoE monitoring.

Considerable work has been done to identify the best way to deal with censored data (Helsel et al. 2020, Helsel & Lopaka 2006, Snelder et al. 2021). However, none of the reported work has dealt with ratios. A pragmatic decision was made to remove metal ratios from the analysis when both the total and dissolved metal values were censored. This resulted in the removal of 288 copper and 393 zinc observations from the stream SoE data set (7% and 11% respectively) and 2 copper observations from the stormwater data set (0.1%).

If only one of the attributes was censored, the censored value was replaced with the detection limit, and the ratio was used in the analysis. When only the total metal value is censored, the metal ratio must be equal to or greater than the estimated value. When the dissolved metal is censored, the actual ratio must equal or less than the estimated value. The numbers and percentages of censored values in the stormwater and stream water data sets are described within sections 3.1.1 and 3.2.1 respectively.

Associated with censoring are the ideas of measurement uncertainty and the propagation of errors[4]. Assuming that the 2017 LoD is a measure of random error, the estimated errors are ± 90% for the copper ratio, and for the zinc ratio, it is ± 45%. This assumes metal concentrations are at the median value of the SoE data. If ultra-trace methods were used, the errors would be ± 35% for the copper ratio and ± 15% for the zinc ratio. Random errors of this scale are not show stoppers. However, it does mean there is a high noise-to-signal ratio which might obscure some of the factors determining metal ratios (and differences between these in space, season or flow).

2.3 Analysis

The analysis uses two approaches to achieve the study's objectives. These approaches are Exploratory Data Analysis (EDA) and statistical modelling, and the methods we applied are discussed below; the outputs are presented together in the Results and Discussion section. The analysis uses the R version 4.0.5 (R Core Team 2021) statistical computing environment. Several simplifying assumptions and decisions were made to ensure the investigation was carried out efficiently and effectively. These are:

- Assuming data is drawn from a simple random sample
- Using the same data in the EDA and statistical modelling
- Excluding stormwater from the statistical modelling.

The first assumption simplifies the analysis but is not correct. SoE data is collected through repeated measurements of the same streams, a longitudinal study design. Basically, it means hypothesis tests are more likely to report significant differences, even if the difference does not exist.

The second assumption was made because of the small number of SoE monitoring sites, approximately 40 and less than half have measured flows. It is best practice (Wickham & Grolemund 2017) to undertake the EDA and modelling using different samples of data. But if this had been done, the number of monitoring sites would have been too small to train and test statistical models.

The third assumption, excluding stormwater from the statistical modelling stage, was made because robust modelling would have required a meta-analysis approach (Field & Gillett 2010) to untangle

[4] Explanation as to how the uncertainties were estimated:
Let us call the metal ratio *R*, dissolved metal *D* and total metal *T*. The metal ratio is given by:

$$R = \frac{D}{T}$$

There are errors in the estimates of total(*T*) and dissolved (*D*) metals represented by δT and δD, and errors in the ratio δR. The fraction errors on the metal ratio are given by the following equation:

$$\frac{\delta R}{|R|} = \sqrt{\left(\frac{\delta D}{D}\right)^2 + \left(\frac{\delta T}{T}\right)^2}$$

In this case, we have used LoD as an estimate of the errors, and the median observed total and dissolved values in the calculation. It should be noted that the fractional errors reduce as the total and dissolved values increase, so the fractional errors are lower for the stormwater data than the SoE data.

the effects of different stormwater study designs. Given the available resource and the study objectives, it was decided not to do this.

2.3.1 EDA

EDA uses graphical techniques such as histograms, box plots, scatter plots, and descriptive statistics to characterise data and identify patterns. Principle Component Analysis (PCA) was also undertaken as part of the EDA. PCA helps to disentangle the complex relationships between multiple attributes and summarise them. It does this by taking a complex data set and representing it in terms of Principle Components (PC). The first component (PC1) represents the direction of most variation in the data, PC2 the next highest level of variation and so on. We can then plot out the PC to give a visual representation of the observations and the attributes on a single diagram.

The EDA used the following R libraries, including Tidyverse (Wickham et al. 2019) for the data wrangling. The graphics were produced using cowplot (Wilke 2020), ggfortify (Tang. et al. 2016), ggplot2 (part of the Tidyverse), psych (Revelle 2021), RColorBrewer (Neuwirth 2014) and scales (Wickham & Seidel 2020).

2.3.2 Statistical modelling

Statistical modelling was used to further our understanding of metal partitioning. We used several; methods: Ordinary Least Squares Regression (OLSR), Multiple Linear Regression (MLR), Linear Mixed Models (LMM) and Random Forests (RF) as detailed below. With the exception of RF, these methods allow us to express the relationship between metal partitioning (so-called response variable) and predictors (such as water quality attributes and land use) in the form of a simple equation. Statistical modelling was used to support the EDA as well as to model (predict) the copper and zinc ratios in streams.

OLSR, MLR and LMM are all related approaches. We tell the computer what we think the relationship between the metal ratios is and the computer determines what the model coefficients should be. On the other hand, RF[5] works out both the relationships and what coefficients could be and is a form of machine learning.

OLSR relates one predictor to the response variable, and MLR is an extension that connects more than one predictor to the response variable. When it comes to MLR, there are many combinations of predictors we could choose, over 100 for each of the zinc and copper ratios. We used the Best Subset Selection approach using Mallow's Cp for the decision criterion (James et al. 2021). Best subset selection is a semi-objective approach to identifying the best set of predictor variables.

OLSR and MLR assume that the data is drawn from a simple random sample. As we know, this fact is not true. It means the model output statistics, such as p-values and significance tests, may be incorrect. But we can still use these models to make useful predictions. The prediction accuracy was tested by splitting the data into a test and training set, using the validation approach (James et al. 2021), which provided information on how well the model predicts metal ratios. The training set had 21 SoE sites and the test set 13 sites. The model test sites, chosen at random, were: Avondale Stream, Cascades Stream, Kaukapakapa River, Kumeu River, Lucas Creek, Makarau River, Ngakoroa Stream, Okura Creek, Omaru Creek, Pakuranga Creek, Riverhead Stream, Wairoa River and Waiwera Stream.

[5] Random Forests are based on the concept of a decision tree and are essentially an average of many trees, hence the name forest.

Given that the data were not drawn from a simple random sample, Linear Mixed Models (LMM) (Faraway 2006) were also examined. In theory, LMM can deal with situations of repeated sampling, as with the SoE data, however, the results are harder to interpret than MLR. Importantly, the model diagnostics suggested that the model assumptions had been violated, so LMM were not used extensively in this work.

Given the challenges with MLR and LMM, Random Forest models were also developed. Random Forests (Breiman 2001) is a modelling tool that has been applied successfully to estimating water quality parameters previously in New Zealand (Whitehead 2022). Random forest models often perform better than multiple linear regression in complex data sets with many data points. This method also has a helpful feature that estimates the relative importance of variables, providing an alternative to the best subset selection used in the MLR approach. However, there are a couple of drawbacks: RF is a black box type of model and it is not possible to express the model as an equation, unlike a MLR model. Secondly RF cannot be used for hypothesis testing (although neither could the MLR or LMM in this study).

The predictive performance of the models was reported in terms of the coefficient of determination, r^2. The R libraries used were randomForest (Liaw & Wiener 2002), Lme4 (Bates et al. 2014) for LMM and Leaps (Lumley 2020) for best subset selection.

3 Results and Discussion

This section is in three parts. The first two present the analysis results for stormwater and stream water, respectively and the third compares these results.

3.1 Stormwater results

All data described in this section are for untreated stormwater, collected within or at the end of the piped stormwater network. As described in section 2.2.1, the data were acquired from URQIS and supplemented with data from additional stormwater studies.

3.1.1 Metal ratios in stormwater

The stormwater dataset (URQIS plus additional studies, as specified in section 2.2.1) included over 2000 stormwater event observations of untreated stormwater from urban land uses for copper and zinc. Ratios were calculated from the measurements of total and dissolved metals.

The overall metal ratio summary statistics are presented in Table 3-1. The mean and median values for copper and zinc were lower than the default ratio used in the FWMT modelling, which was 0.676 and 0.688 for copper and zinc ratios, respectively (i.e., FWMT metal ratios result in greater dissolved metal concentration).

Table 3-1: Stormwater sample descriptive statistics for copper and zinc ratios. All data are untreated stormwater from URQIS supplemented with additional stormwater studies as described in section 2.2.1. These figures excluded two copper samples where both total and dissolved results were censored.

Metal ratio	Mean	Standard deviation	CV	Median	Min	Max	5th percentile	95th percentile	n	Count greater than FWMT ratio	FWMT equivalent to Xth Percentile
Cu ratio	0.431	0.250	0.580	0.404	0.002	1.482	0.065	0.846	2182	442	20th
Zn ratio	0.574	0.325	0.565	0.624	0.002	4.737	0.055	0.968	2203	952	43rd

Note: FWMT Cu ratio = 0.676 Zn ratio = 0.688

The range of observed values did include the FWMT partitioning parameter (0.676 for copper and 0.688 for zinc). However, there was a very broad spread in the ratios, as illustrated in Figure 3-1. For copper, the distribution of ratios was somewhat right-skewed, with the mean and median less than 0.5. For zinc, the ratios were almost uniformly spread between 0 and just under 0.8, but with a cluster of data between 0.8 and 1. There was greater variance in the ratios for zinc - a standard deviation of 0.325 as opposed to 0.250 for copper - although the relative variation as demonstrated by the coefficient of variation (CV, standard deviation relative to the mean) was similar at 0.580 and 0.565 for copper and zinc respectively.

There are also examples in the dataset of ratios greater than one (which implies greater dissolved metal than total), which probably relates to uncertainties in the sampling and laboratory analysis. However, values greater than one were the exception and 90% of the ratios determined from the observations were between 0.065 and 0.846 for the copper ratio and between 0.055 and 0.968 for the zinc ratio (Table 3-1).

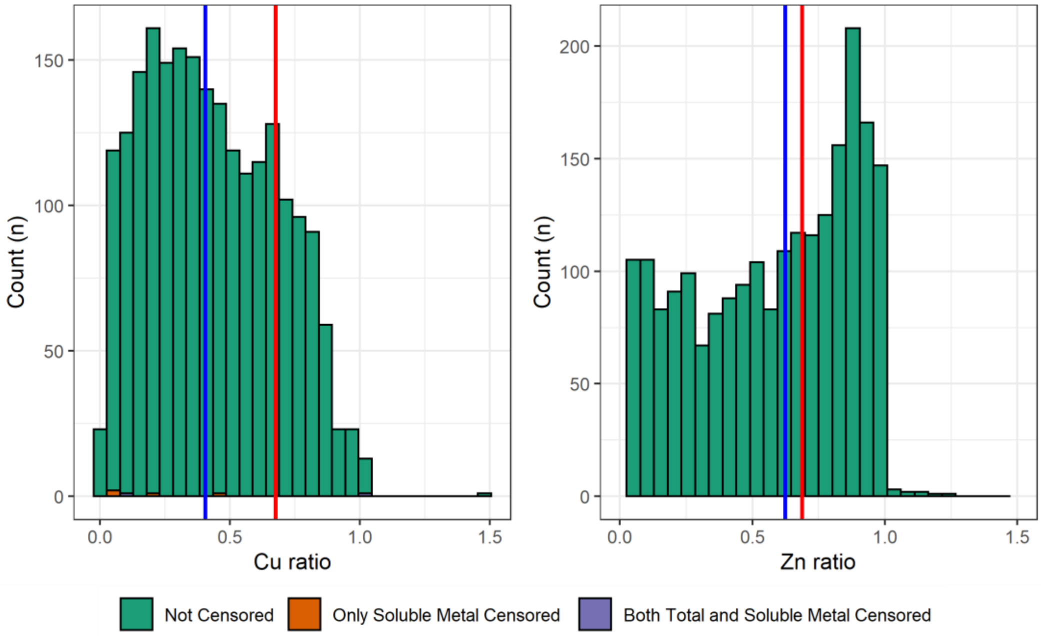

Figure 3-1: Histogram of metal ratios in stormwater data. All data are untreated stormwater, from URQIS supplemented with additional stormwater studies as described in section 2.2.1. The red line indicates the metal partitioning ratio used in the FWMT model, which is 0.676 for copper and 0.688 for zinc. The blue line is the sample median; 0.404 and 0.624 for copper and zinc, respectively. Most of the samples are uncensored. There is a small number of results with ratios greater than one. Three of the zinc results (not shown) have ratios greater than 1.5.

3.1.2 Variation in total and dissolved metals

Figure 3-2 illustrates the variation of total and dissolved metal concentrations. There is some relationship between the two, as dissolved metals are a subset of total metals and are thus constrained by the total metal concentrations, as illustrated by the black line in Figure 3-2. However, the scatter in the data further demonstrates the variation in the ratio, particularly for copper. The Pearson correlation coefficient for total and dissolved copper was 0.425, compared to 0.888 for zinc. For zinc, the ratios vary considerably (e.g., 0.5 – 1) when the dissolved and total zinc concentrations are less than 0.2 mg/L, but at concentrations higher than 0.2 mg/L, the ratio is more frequently between 0.7 and 1.

The variation in the observed concentration and partitioning of metals reflects the variety of urban land uses and surface types included in this data set. As the samples are usually taken close to where the contamination was generated, there is little opportunity for the composition of the stormwater to change, for example, through processes such as sedimentation and the loss of particles. Differences in ratios depending on stormwater sources are investigated in the next section.

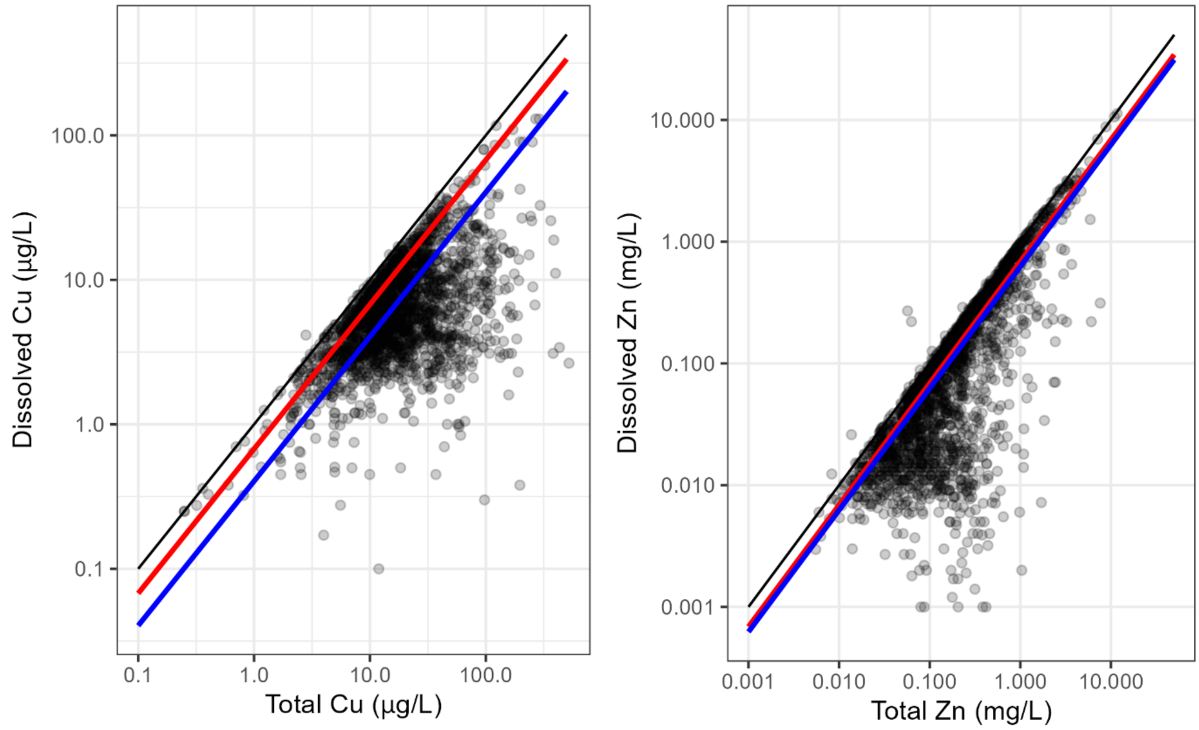

Figure 3-2: Scatter plots of total and dissolved metals in stormwater. All data are untreated stormwater from URQIS supplemented with additional stormwater studies as described in section 2.2.1. The black line is 1:1, the red line is the default ratio used in FWMT and the blue line is the sample median. Note the different scales on the graphs, with zinc having higher concentrations than copper.

3.1.3 Differences due to catchment land use/land cover

This section explores the observed ratios described above in relation to different urban land uses/land covers (referred to as land use in this report). Nine urban land uses were included in the analysis: low-density residential, medium-density residential, commercial, CBD, light industrial, car parks, Roads 5000-20,000 vpd (vehicles per day), Roads > 20,000 vpd, Roads(not classified) and Roof. Although there were also data for mixed and heavy industrial land uses, these were excluded as there were less than 10 data points for copper ratio.

There is variation in the observed metal ratios by land use, as shown in Figure 3-3. The highest median copper ratio was observed in stormwater from car parks and the lowest in stormwater from roads (not classified). The interquartile range (IQR), the middle 50% of data points indicated by the coloured boxes, generally did not include the default ratio used in the FWMT. The exceptions were car parks and low-density residential sites.

Variation between land uses was also noted in the zinc ratio, with roofs having the highest ratio, with a median close to 1 and the least variation. Roads 5000-20,000 vpd and roads >20,000 vpd had the lowest ratios, close to 0.25. The interquartile range for zinc ratios included the FWMT default model value in all cases, except for roads > 20,000 vpd, roads 5000-20,000 vpd, roads (not classified) (all IQR below the model value), and roof (IQR above the model value).

The ratios shown in Figure 3-3 reflect our current knowledge and understanding of copper and zinc sources in stormwater. In roof runoff, zinc from galvanised roofing is generated through the weathering (or corrosion) of the zinc-coating. Similarly, copper from copper roofing, guttering and downpipes is also generated through weathering. The weathered form of the metal is then dissolved when rainwater flows across the roof (Charters et al. 2016, Good 1993, Kingett Mitchell Limited and Diffuse Sources Limited 2003, Odnevall Wallinder & Leygraf 2017, Pennington & Webster-Brown 2008). As the amount of sediment in rainwater and on roofs is low, there is minimal opportunity for that dissolved zinc (or copper) to adsorb to particulates. Light industrial land uses typically have a high proportion of zinc-based roofing in the catchment, and it is not surprising that the zinc ratio for this land use is close to that of roofs.

In contrast, metal ratios in road runoff are much lower. This reflects that copper and zinc are predominantly present in a solid form on vehicles, e.g., within brake pads (copper) and tyres (zinc) (Legret & Pagotto 1999, Semadeni-Davies et al. 2021, Timperley et al. 2005). Wear of the brakes and tyres results in the formation of small particles that are deposited on the road. Rainwater subsequently dissolves some of the copper and zinc from these particles, but a proportion can remain within the original matrix or be re-adsorbed to other particles present in the road runoff (Herrmann et al. 1994) and hence is measured as the particulate form.

Land uses such as low-density and medium-density residential land include a mixture of land covers (i.e., roofs, roads, paved areas, pervious surfaces) in the catchment, and stormwater from these catchments tends to have ratios that reflect that mixture – that is, mid-way between roads and roofs.

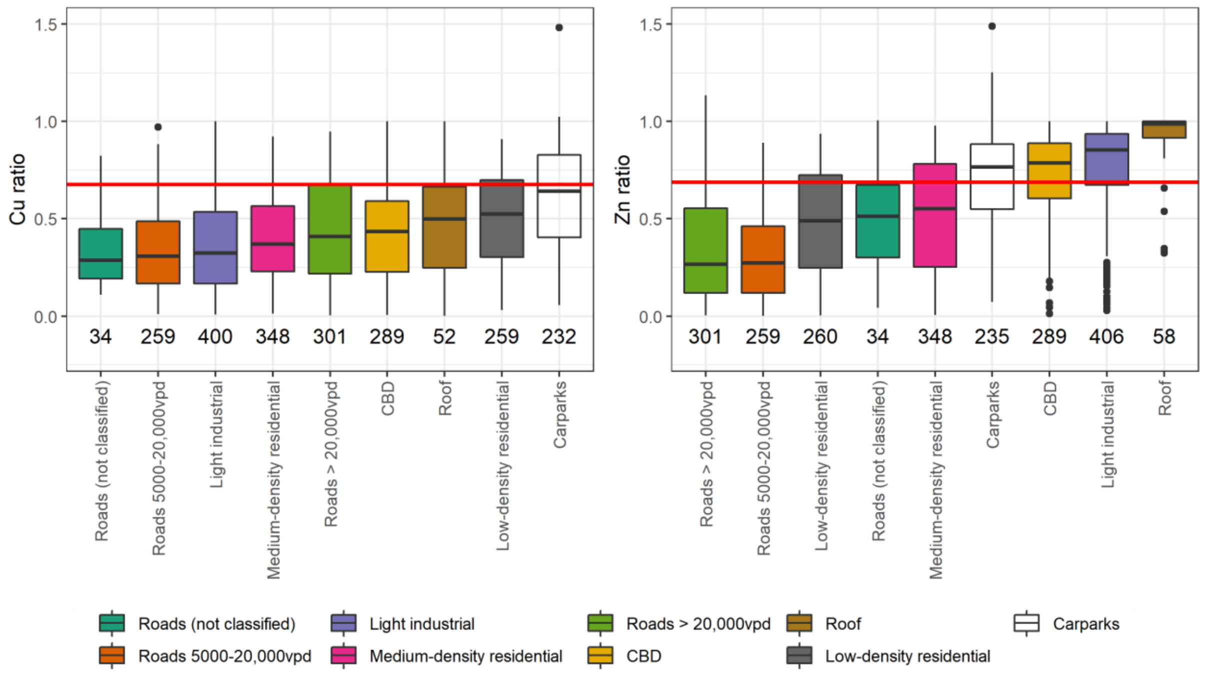

Figure 3-3: Boxplot of stormwater metal ratios by land use. The ratios vary by land use, both for zinc and copper, but not in the same way. Note the zinc y-axis has been truncated at 1.5. The red line is the default value used in FWMT. All data are untreated stormwater from URQIS supplemented with additional stormwater studies as described in section 2.2.1.

As well as differences in the metal ratios by land use, there are also differences in the metal concentrations . For copper, there are similarities between the observed total copper concentration for most land uses (Figure 3-4), except roofs and carparks, which had lower concentrations (based on median and interquartile ranges). For most land uses, the soluble copper concentrations were consistently much lower than the total copper concentrations. Only in the case of roofs, carparks and low-density residential land uses did the interquartile range of the dissolved copper concentrations overlap with the total copper concentrations, as previously shown by the higher ratios for these three land uses.

The highest concentrations of total zinc were found in stormwater from light industrial sites and in roof runoff and the lowest in runoff from carparks.Almost all the zinc from roofs was in dissolved form, as previously shown through the high ratio (Figure 3-3). What is interesting to note is the differences between the roads: Roads > 20,000vpd and Roads 5000-20,000 vpd appear to be quite similar in both total zinc and dissolved zinc. However, the Road (not defined) classification has higher total and dissolved metals than these other roading sources. The latter data set is from road runoff from Christchurch and suggests differences between studies, so some caution needs to be taken when generalising these results.

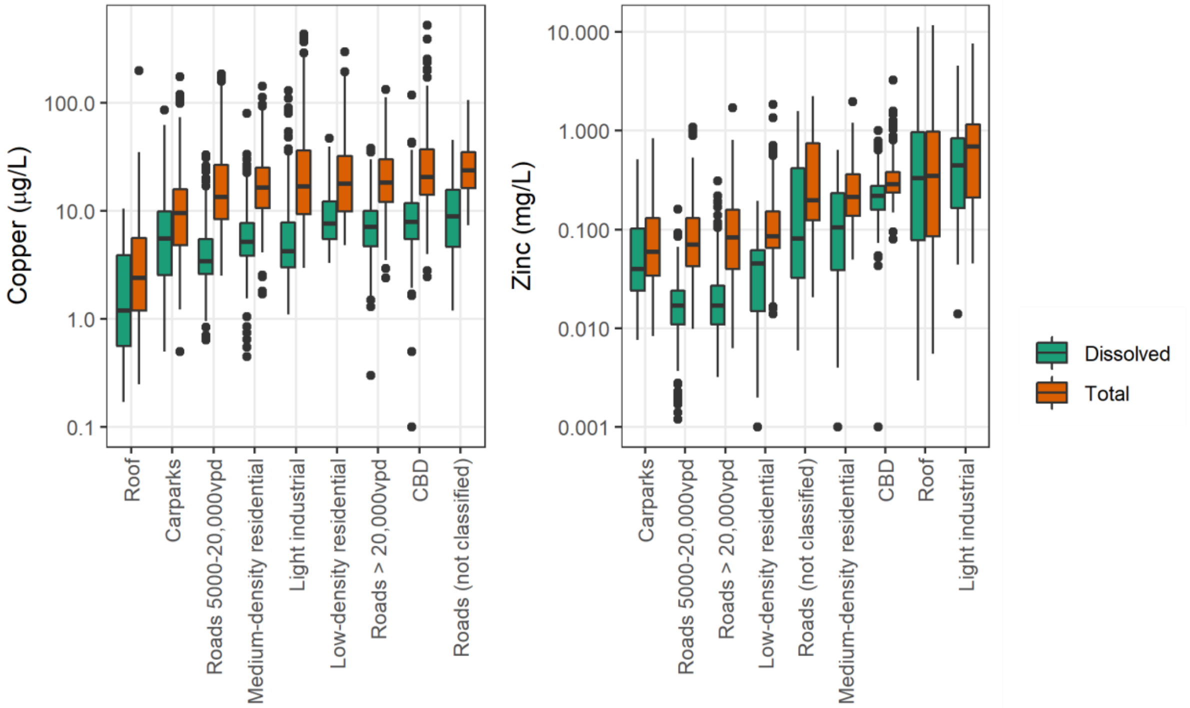

Figure 3-4: Boxplot of total and dissolved metal concentrations in stormwater, categorised by dominant land use in catchment. All data are untreated stormwater from URQIS supplemented with additional stormwater studies as described in section 2.2.1. Note log-scale on y-axis. Copper plot arranged by ascending median concentration of total metal.

3.1.4 TSS

This section investigates whether copper and zinc ratios are related to suspended solids. Figure 3-5 and Figure 3-6 illustrate that higher levels of TSS are associated with lower ratios for both copper and zinc. The best fit line is a curve that takes a sigmoidal form as it is constrained between the value zero (all the metals are in particulate form) and one (all metals in dissolved form). There are differences between land uses in metal ratios and TSS.

TSS can be generated from various sources and processes in the urban environment. For example, as was noted above, vehicular traffic on roads generates TSS by wear of tyres, brakes, and road abrasion (Muller et al. 2020). Construction activity, particularly earthworks, can also generate TSS. There is little opportunity to generate TSS from metallic surfaces, explaining why roofs have the lowest observed TSS and the highest zinc ratio. It is not clear why car parks have lower TSS than other sites. It possibly reflects lower speeds and less wear and tear on vehicles compared to roads or different types of surfaces.

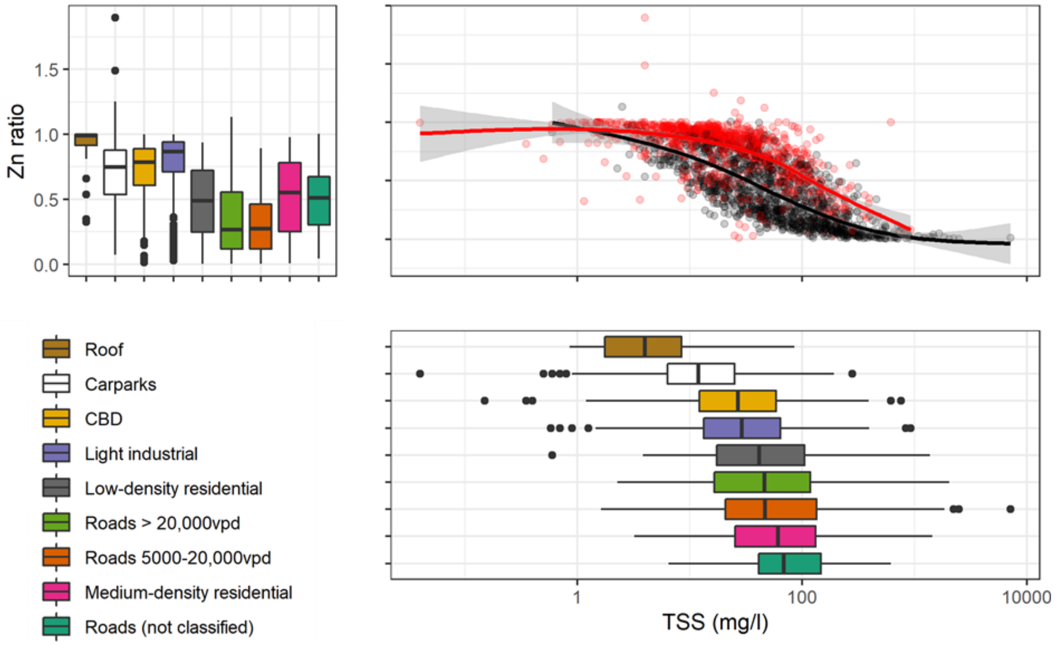

Figure 3-5: Zinc ratio and Total Suspended Solids (TSS) for stormwater All data are untreated stormwater from URQIS supplemented with additional stormwater studies as described in section 2.2.1. Red dots are from sites with high ratios: roof, car parks, CBD and light industrial land uses; black dots are data from other land uses. Red line is the best fit for the group with the higher zinc ratio, and the black line is associated with the lower zinc ratio group.

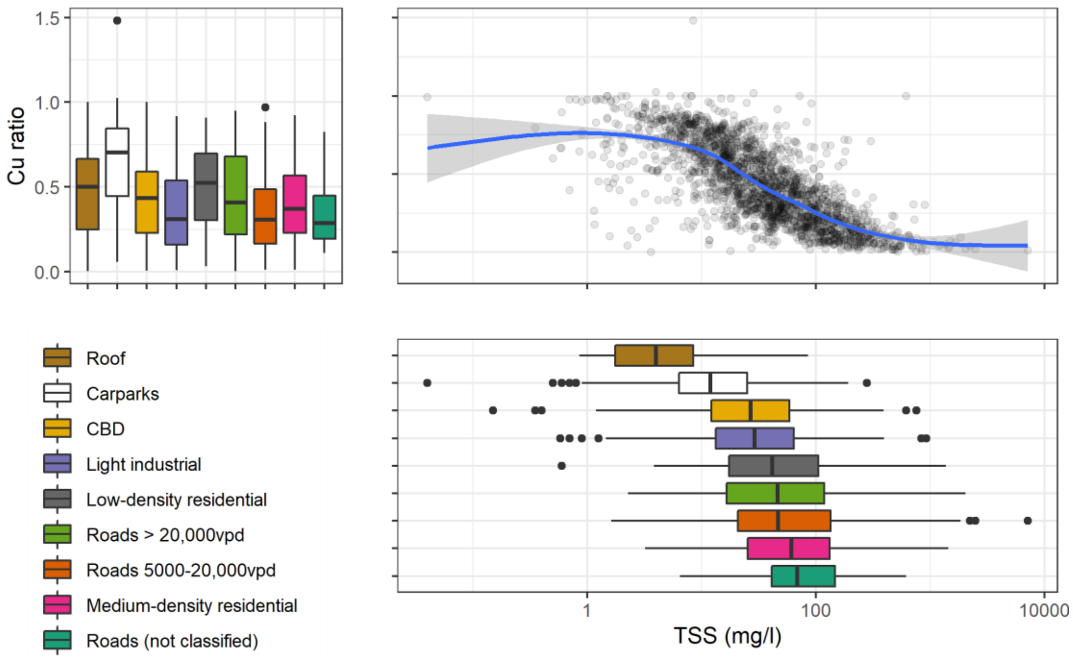

Figure 3-6: Copper ratio and Total suspended solids. All data are untreated stormwater from URQIS supplemented with additional stormwater studies as described in section 2.2.1. Black dots are observations, and the blue line is the best fit line through all the points.

Roofs, car parks, CBD and light industrial sites (red dots in Figure 3-5) tend to have TSS concentrations from ~2- 50 mg/L and higher zinc ratios than the second group, as illustrated by black dots. The second group, made up of roads, light industrial and residential, had slightly higher TSS (20-200 mg/L) and lower zinc ratios. Both groups show a trend of decreasing metal ratios with increasing TSS.

3.2 Stream results

All data described in this section are for stream water, as collected monthly through the Auckland Council SoE programme. The data cover the period 2003 to June 2021 and differ for each site, due to the different period of metal monitoring at each site. As with all SOE monitoring programmes, the sampling occurs over a range of different stream flows, but does not include the highest flows that occur very infrequently.

3.2.1 Metal ratios in streams

The overall summary statistics for copper and zinc ratios for streams in the Auckland Council SoE programme are presented in Table 3-2. The median and mean values of the copper ratio were slightly higher than the default value used in the FWMT of 0.676. The median and mean values for zinc were similar to the default value of 0.688. Slight differences between the median ratio here and the FWMT default value are expected. Although both are based on the SoE monitoring, there are several differences in the data sets. The FWMT default value was calculated from data collected up to December 2016, from 24 sites that included metal measurements, of which 11 were located within urban catchments. This report includes sampling from 34 streams up until June 2021 and includes a larger number of data points from rural streams, including eight additional sites where metals were added to the monitoring programme after 2017.

The distributions of these ratios are displayed in Figure 3-7. Ninety percent of the ratios took the value 0.383 to 1.00 for copper and 0.273 to 1.00 for zinc, though there were some ratios greater than one, and some values were censored.

Overall there were 4,016 copper and 4,08 zinc observations for total and dissolved metals. Of these, 288 copper and 393 zinc observations were censored for both total and dissolved metals, and these were excluded from the analysis. There were 169 copper and 288 zinc ratios where dissolved metal concentrations were censored and 29 ratios for each metal where the total metal concentration was censored, and in both situations the censored value was replaced with the detection limit. In all, 3728 and 3615 copper and zinc ratios were analysed.

Table 3-2: Stream water sample descriptive statistics for copper and zinc ratio. All stream data from Auckland Council SoE dataset. These figures exclude 288 copper and 393 zinc samples, where both total and dissolved results were censored.

	Mean	Standard deviation*	CV*	Median	Min	Max	5th percentile	95th percentile	n	Count greater than FWMT ratio	FWMT equivalent to Xth Percentile
Cu ratio	0.706	0.169	0.241	0.710	0.006	3.200	0.383	1	3,728	2,158	58th
Zn ratio	0.686	0.206	0.315	0.667	0.013	56.522	0.273	1	3,615	1,672	46th

- * used trim mean to estimate standard deviation and coefficient of variation CV to exclude the top and bottom 2.5% of values
- Note: FWMT Cu ratio = 0.676 Zn ratio = 0.688

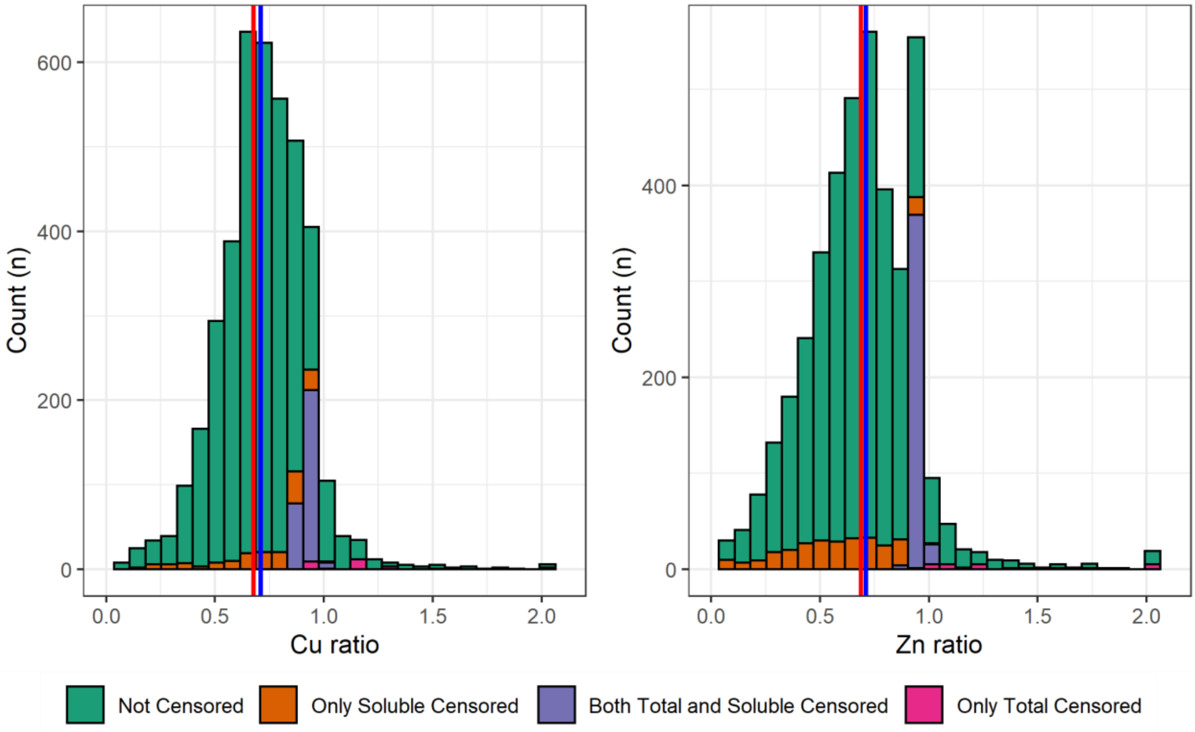

Figure 3-7: Histograms of metal ratios in stream water. All data from Auckland Council SoE dataset (2003 – 2021, depending on site, see Appendix A). The red line indicates the metal partitioning ratio used in the models. The blue line is the sample median (for all samples). Most of the samples were censored. There are a small number of results with ratios greater than one, and for the purposes of this figure, all values with ratios greater than 2 are given the value 2.

3.2.2 Variation in total and dissolved metals

There is variation in the concentrations of total metals and dissolved metals as well as variation in metal ratios. The scatter plots in Figure 3-8 illustrate a range of observed total and dissolved metal concentrations. Higher levels of total metals tend to be associated with higher levels of dissolved metals. The Pearson correlation coefficient was 0.869 for copper (n = 4,016) and 0.946 for zinc (n = 4,008) based on the log-transformed data. There is much less variation in the stream data set ratios than in the stormwater data set. The lower variation can be expected for two reasons. Firstly metals within each stream are typically from a range of sources, particularly for the urban streams, which receive runoff from road, roofs and other impervious surfaces, making the stream an average of multiple inputs. Secondly, in streams, there may be time for physical, chemical and biological processes to alter the metal composition of the water. Whilst there are explanations for the variation based on what happens in streams and stormwater, the fact that there are some cases in the top left quadrant above the black line for both metals implies there is more dissolved metal than total metal in the samples. Although not physically possible, these discrepancies illustrate that there is noise in the data, possibly due to experimental error or measurement uncertainty.

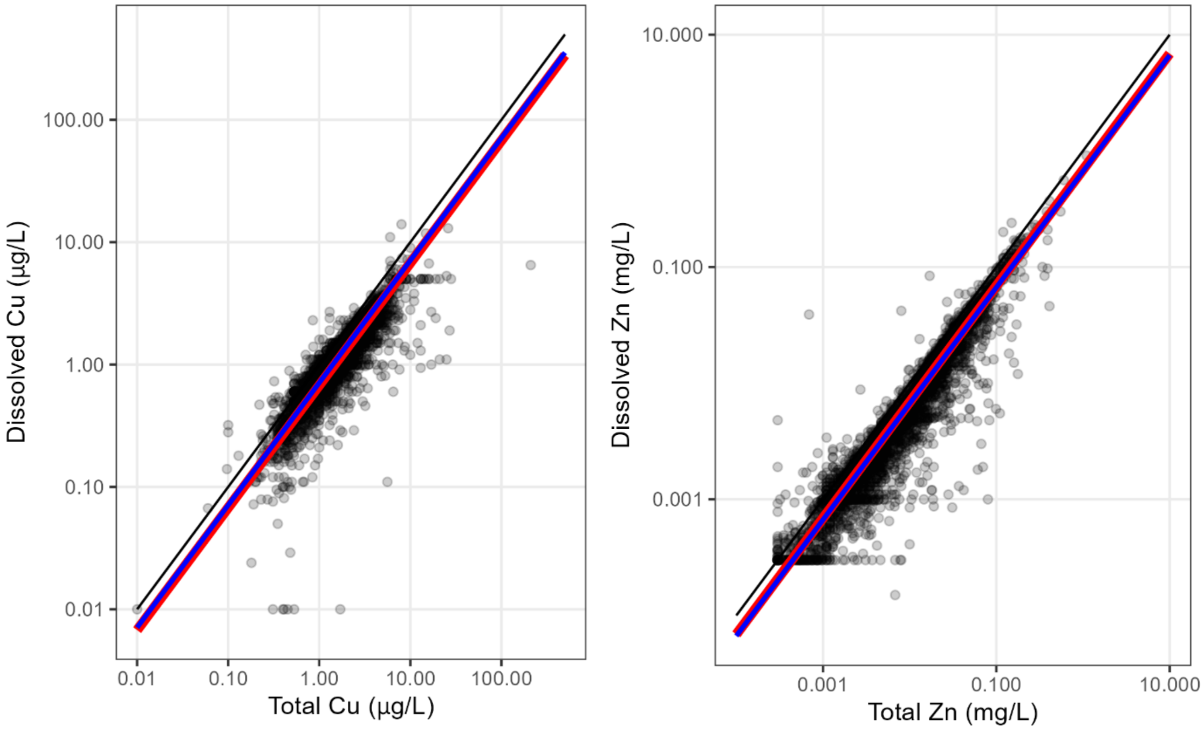

Figure 3-8: Scatter plot of total and dissolved metal in stream water. All data from Auckland Council SoE dataset (data from 2003 – 2021, depending on site, see Appendix A). The black line is 1:1, the red line is the default ratio used in FWMT, and the blue line is the sample median. The blue line plots over the top of the red line (which has been made thicker than the blue), illustrating the similarities in observed and default values.

3.2.3 Principal Component Analysis

As well as measuring zinc and copper, a number of other variables are monitored in the SoE programme. A summary of key water quality variables measured and used in this study are presented in Table 3-3.

Two PCAs were carried out to understand how key water quality variables relate. One PCA for copper ratios and the other for zinc ratios (Figure 3-9). To simplify the figures, the PCA was applied to a subset of attributes: total metals, metal ratio, TSS, DNPOC, electrical conductivity, pH and water temperature[6]. Because Auckland Council has only recently started monitoring dissolved non-purgeable organic carbon (DNPOC), this PCA analysis is based on a subset of data, from November 2017 onwards (n = 1,138 for copper and n = 1,337 for zinc).

The first two principal components (PC1 and PC2) accounted for approximately half of the observed variance in both datasets. Zinc and copper ratios load negatively onto PC1 and slightly positively on PC2. TSS, DNPOC and total metals load positively onto PC1 and slightly negatively on PC2, suggesting an inverse relationship between these variables and the metal ratio. A second group of variables, water temperature, pH and electrical conductivity, all load strongly onto PC2. For both metals, land use was distinguished by PC1 with higher values for urban, and lower values for reference, and the streams in the rural & lifestyle category falling in-between the two end members (Figure 3-9).

[6] Disolved metals were not included in the analysis, as the combination of dissolved and total metal explains all the variation in metla ratio. We focussed on total metals, as the FWMT simulates the total metals.

Table 3-3: Descriptive statistics and monitoring site count results for each variable. All data from Auckland Council SoE dataset (2003 – 2021). The table includes all results. Note that not all variables were measured at each observation/sampling occasion due to changes in the programme over time.

Parameter	Mean	Median	5th percentile	95th percentile	Sample count(n)	Site Count(s)
Ca – soluble (mg/L)	12.9	12	4.9	25	1,462	34
Cu – dissolved (mg/L)	0.00124	0.00095	0.00032	0.0032	4,020	34
Cu – total (mg/L)	0.00196	0.00136	0.00049	0.0056	4,017	34
DNPOC (mg/L)	3.87	3.4	1.1	7.7	1,462	34
Elec Cond Field (mS/cm)	0.221	0.201	0.119	0.381	5,951	35
Elec Cond lab (mS/cm)	20.5	18.7	11.3	33.8	685	23
Mg – soluble (mg/L)	5.76	4.9	2.6	11.7	1,462	34
pH (field)	7.19	7.2	6.43	7.91	4,565	34
pH (lab)	7.41	7.4	6.9	7.9	3,904	35
Total Alkalinity (mg/L)	45.8	39	19.3	90.1	1,539	34
Total hardness (mg/L)	56.7	51	25	104	1,224	34
TSS (mg/L)	8.27	4	1	27	6,342	35
Water Temp (°C)	15.2	14.9	10.3	21	6,314	35
Zn – dissolved (mg/L)	0.0126	0.0035	0.00044	0.05	4,013	34
Zn – total (mg/L)	0.019	0.006	0.000816	0.074	4,014	34
Flow (m^3/s)	0.632	0.0765	0.0023	3.08	2,089	12

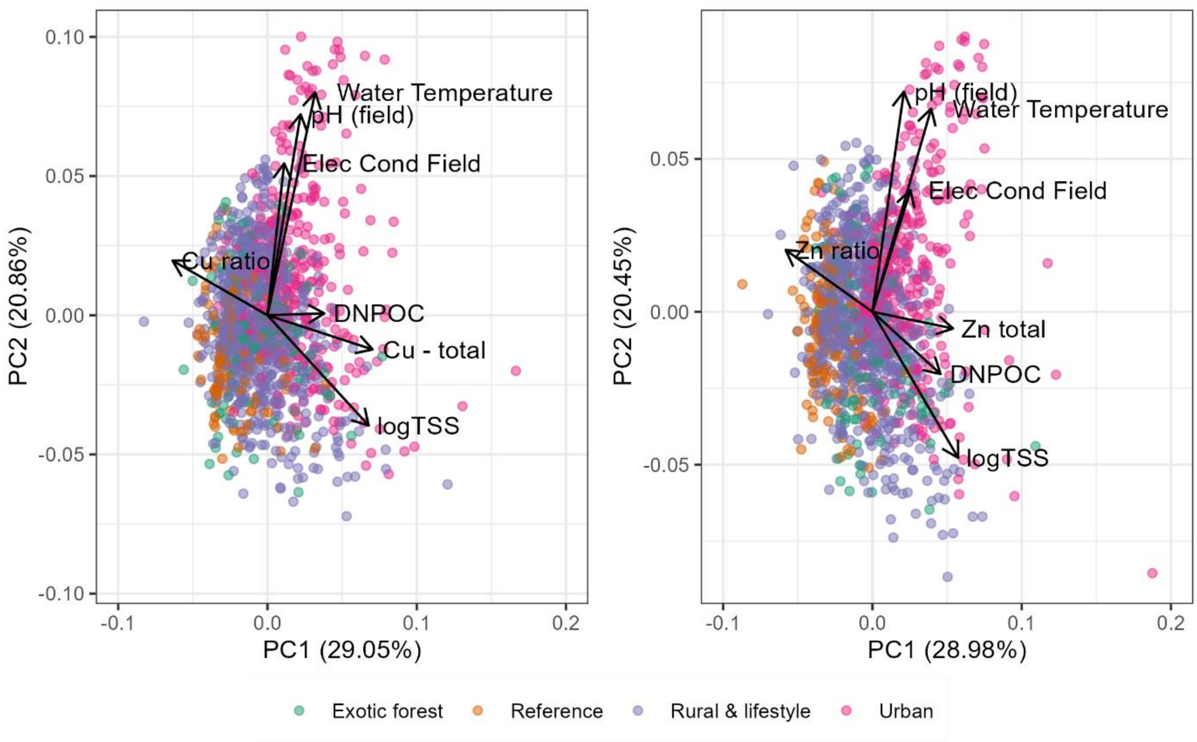

Figure 3-9: Principal Component Analysis (PCA) for copper and zinc based on AC SoE dataset (November 2017-June 2021).

Other versions of the PCA analyses were carried, out but are not shown here. These investigations included the additional variables alkalinity, hardness, total calcium and total magnesium. In all cases, these variables were closely associated with water temperature, pH and electrical conductivity and appeared independent of metal ratios.

Another way to look at the data is through pair plots shown in Figure 3-10 and Figure 3-11. The numbers in the upper right quadrant are the Spearman rank correlation coefficients. The zinc ratio was log-transformed to align with the regression analysis presented later.

There are some commonalities between copper and log-transformed zinc ratios. The following sections delve deeper into the bivariate relationships with strong correlations (both positive and negative) between continuous variables and metals and landuse. The variables considered were:

- Sample site and land use
- Flow
- Season
- TSS
- Total metal

DOC was not investigated further due to the smaller data set available as regular monitoring started in November 2017.

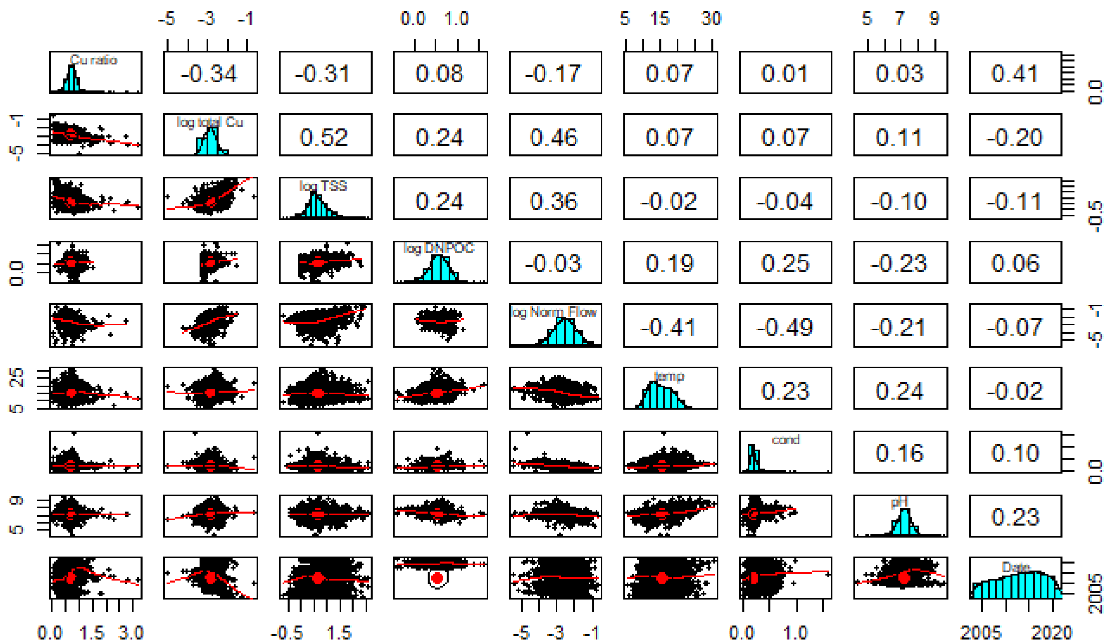

Figure 3-10: Pair plots for copper ratio based on AC SoE dataset. Data from 2003 to 2021, depending on variable included (see Appendix A). The diagonal from the top left to the bottom right contains histograms of nine variables, some of which have been log-transformed as indicated by the name. The plots on the bottom left quadrant are scatter plots of pairs of attributes. The black dots are the observations. The large red dots are the mean of observations. The red line is a smoothed "best fit" line. The numbers on the top-right quadrant are Spearman rank correlation coefficient, a measure of association between each pair of variables.

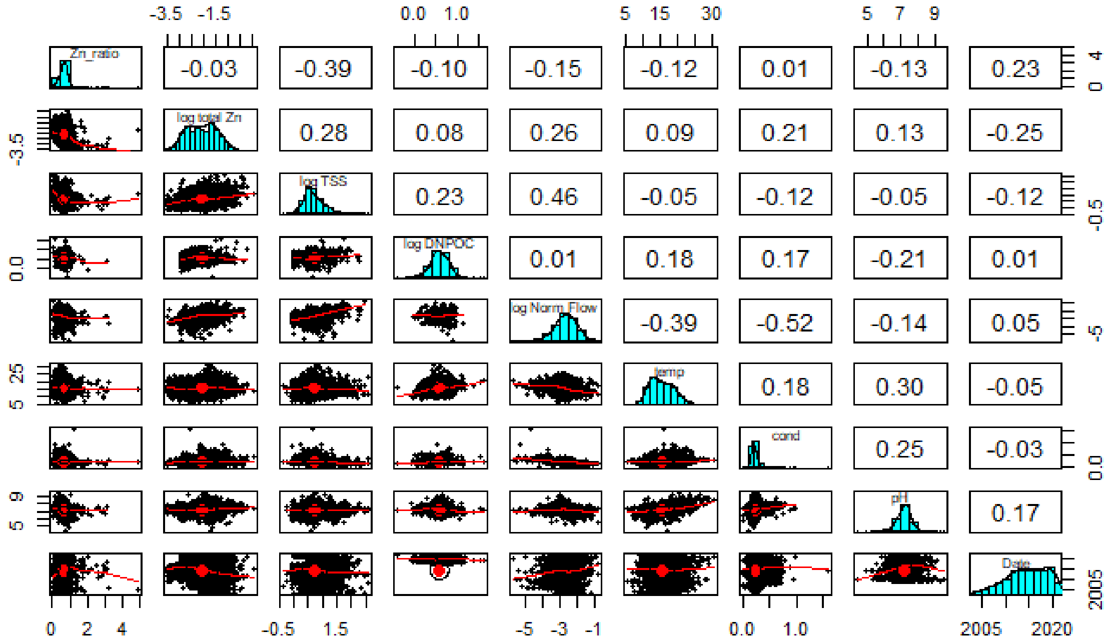

Figure 3-11: Pair plots for the log zinc ratio based on AC SoE dataset. Data from 2003 to 2021, depending on variable included (see Appendix A). See the explanation in Figure 3-10 for a full description. Note the different number of points between the scatter plots on the lower left, particularly the DNPOC/data graph, illustrating that the measured attributes has changed over time.

3.2.4 Variation by stream site and catchment land use

There was variation in the AC SoE dataset metal ratios spatially between and temporally within sites (Figure 3-12 and Figure 3-13). For most sites, the interquartile range (shown by the coloured boxes) includes the default metal ratio used in the FWMT. The zinc interquartile range for all sites included the default ratio (0.688) except for one site with consistently lower ratios and two sites with consistently higher ratios. There was a slight tendency for streams categorised as rural & lifestyle to have higher copper ratios than urban, and for the interquartile range to be above the FWMT default ratio in some of these sites. However, there are exceptions, such as Okura Creek, a rural and lifestyle site - this site has one of the lowest median copper ratios (0.667), which was close to that of the FWMT default ratio (0.676). Conversely, there was no obvious land use pattern for zinc ratios, with urban and rural and lifestyle sites having a broad range of observed zinc ratios (Figure 3-13).

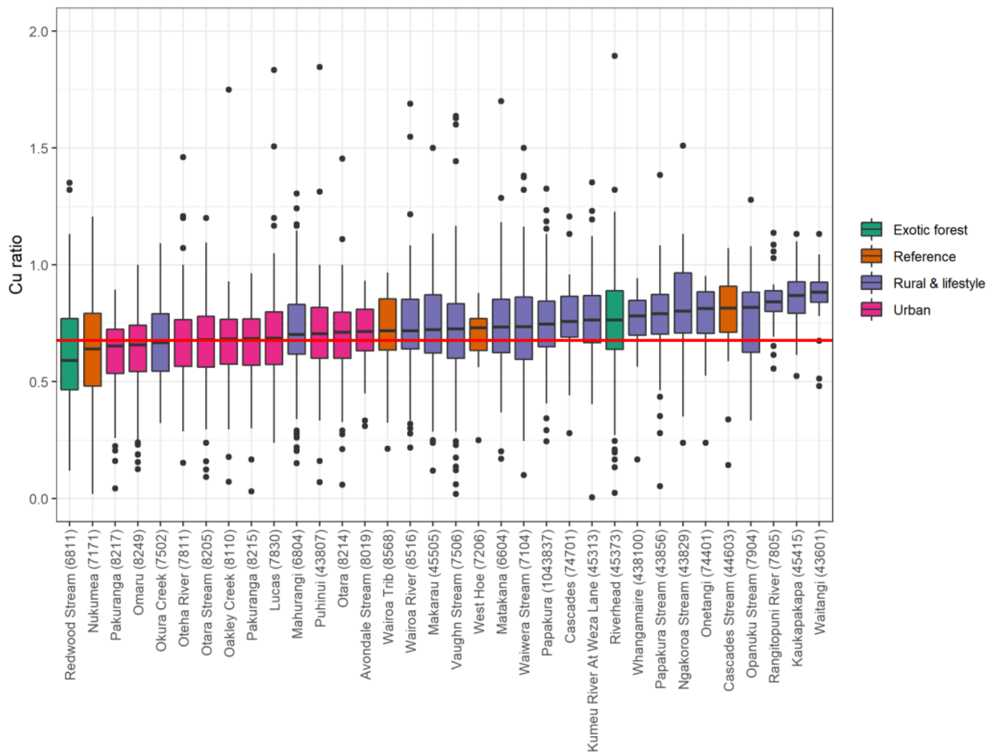

Figure 3-12: Boxplot copper ratio by monitoring site based on AC SoE dataset . Data from 2003 to 2021, depending on site (see Appendix A). The red line is the default setting used in the FWMT, and the box colours refer to the land cover classification used in SoE reporting.

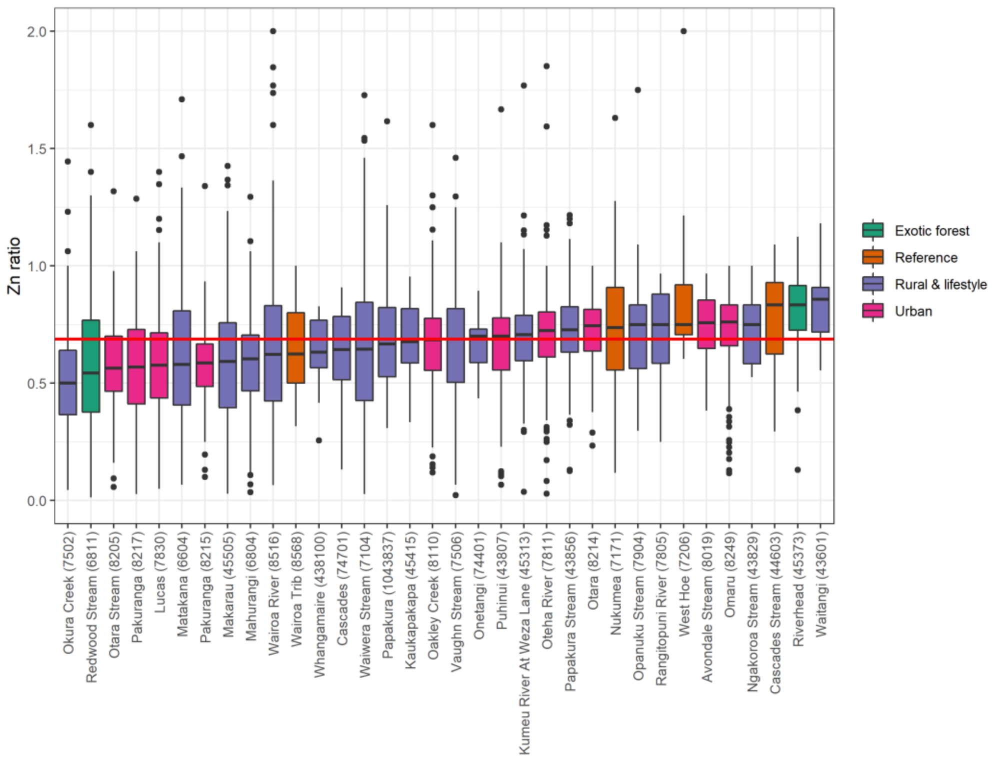

Figure 3-13: Boxplot of zinc ratio by monitoring site based on AC SoE dataset. Data from 2003 to 2021, depending on site (see Appendix A). The red line is the default setting used in the FWMT and the box colours refer to the land cover classification used in SoE reporting.

Ordinary Least Squares Regression (OLSR) demonstrated that land use (based on the four categories) explained about 3% of the observed copper ratio variance. It was noted that there were statistically significant (but possibly not practically significant) differences between land uses ($p < 0.001$). Rural and lifestyle and reference sites had higher copper ratios than urban sites. When including the sampling site as a blocking factor[7], 7% of the variance was explained, suggesting site-specific factors were as important as land use.

Focusing on the zinc ratio, OLSR demonstrated that land use (based on the four categories) explained about 1.7% of the observed zinc ratio variance. It was noted that there were statistically significant (but again, possibly not practically) differences between land uses ($p < 0.001$). Reference sites had higher zinc ratios than urban sites, and there was no difference between urban and rural and lifestyle. When including sampling site as a blocking factor, the variance explained increased to 10%.

Consideration was given to defining land use in terms of the area (ha) of each of the categories used in the FWMT (developed[8], forest, horticulture, open space, pasture, other). However, this approach did not give additional insights or explain more of the observed copper variance than the four land use scheme of exotic forest, reference, rural and lifestyle and urban.

Most sites were urban or rural and lifestyle with only a handful of sites downstream of other land uses. It was decided to classify sites as either urban or non-urban for the remaining analysis.

Although there are differences in the metal ratios between land use, it only explains a small fraction of the observed variation in metal ratios. Some of the variation can be explained by differences between individual sites. However, there is still variation in metal ratios within each site.

3.2.5 Variation by flow

Streamflow is measured at or close to 14 of the SoE water quality monitoring sites. As described in the method section, two approaches were used to compare flows, which vary between sites and depend on factors such as the size of catchment, rainfall, land use, and geology. Briefly, the first approach categorises flows at the time of monthly grab-sampling as “high” or “low”. High flows were those flows of the ‘Highest 10%’ and low flows were those of the ‘Lowest 50%’. The second approach normalises flow on a scale from zero to one, and the normalised flow at time of monthly grab-sampling is used to compare between sites. Note, though both these approaches allow comparisons, they can hide the impact of small storm flow events in summer or after dry weather, which may deliver high levels of metals to a river but do not cause the flow to be “high” compared to the overall average.

Figure 3-14 illustrates a general tendency for the copper and zinc ratios to be lower (meaning a lower proportion of dissolved metal) during high flow (orange box) than low flow (green box). The boxes that represent the interquartile range overlap for both high and low flow, implying some similarity in metal ratios during different flow conditions. Furthermore, the pattern of low metal ratios during high flow is not universal across sites. For two sites, Lucas Creek and Wairoa River, the zinc ratio appears to be quite different at high and low flows. In addition, Opanuku Stream and West Hoe Stream have higher zinc and copper ratios during high rather than low flows. Still, it should be noted that there are a limited number of samples at these sites.

[7] Blocking factors are variables which have an effect on the outcome but is not if direct interest. In this case we are not interested in sampling site but the upstream landuse.
[8] Where Developed = Paved_Commercial + Paved_Industrial + Paved_Residential + Roofs + Roads_Urban + Pervious_Urban, Forest = Forest Horticulture = Horticulture OpenSpace = Open_Space, Pasture = Pasture, Other = Water + OSWW + Roads_Rural

The high/low flow grouping on its own could explain 6% of the observed copper and <1% of the observed zinc variance. However, this increased to 13% and 49% of the observed copper and zinc variance when interactions between sites and flow were included. This suggests that site-specific flow data are required to explain variation in the metal ratios.

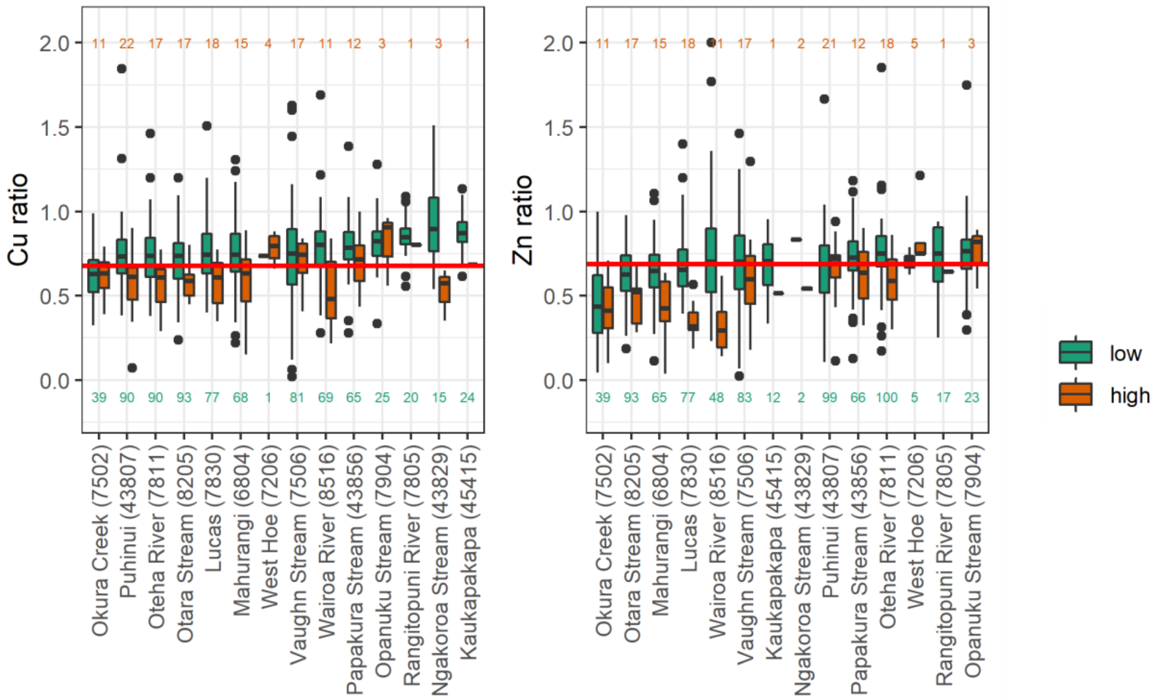

Figure 3-14: Boxplot of the metal ratios by flow for each AC SoE monitoring site. Data from 2003 to 2021, depending on site (see Appendix A). The red lines are the default FWMT levels. Green numbers are the number of observations during low and orange numbers are counts during high flow. Sometimes counts differ between metals because of censoring.

Expanding on the point of differences between sites, by delving deeper into the data, relationships between metal and normalised flow are presented in Figure 3-15. Each line represents a different site. The lines assume a linear relationship between metal ratios and log-transformed normalised flow. Most sites show a decreasing ratio with increasing flow, particularly for the copper ratio. However, a couple of non-urban sites show ratios increasing with the flow. The lines for the urban sites also appear to be more tightly packed together than for the non-urban sites.

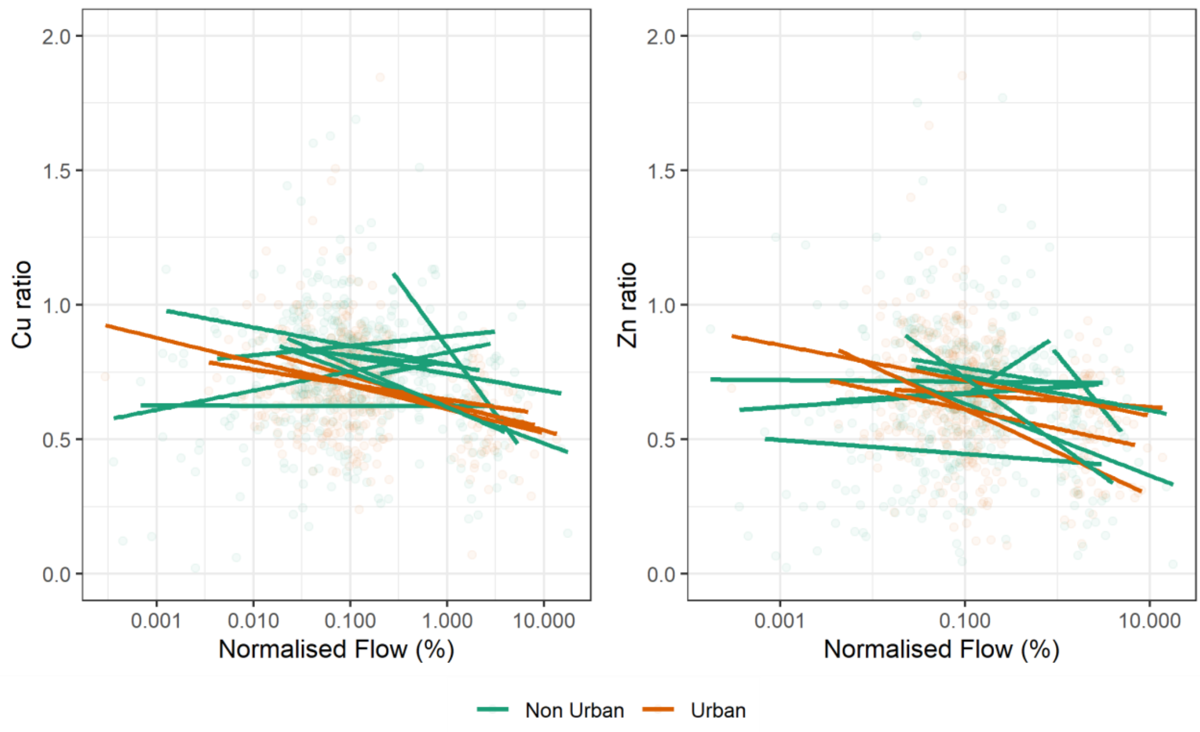

Figure 3-15: Relationship between metal ratio and normalised flow at 14 AC SoE sites . Data from 2003 to 2021, depending on site (see Appendix A). Lines are regression lines for each stream and assume that the metal ratio is proportional to the log of the normalised flow. In general, the ratio goes down with the increasing flow.

In summary, metal ratios tend to be lower (more particulate metal) during high flows and higher (more dissolved metal) in low flows. Though there is a general trend, there are differences between sites.

3.2.6 Variation by season and time

The SoE dataset covers the period 2003 to 2021. When classifying observations into four seasons (spring, summer, fall and winter using the classification and terminology from Table 4-2 of Auckland Council (2020)), there were only minor differences in the metal ratios from season to season (Figure 3-16). In the case of copper, samples from non-urban streams had slightly higher median ratios in spring and summer than in fall and winter, and the differences in ratios were less pronounced for the urban monitoring sites. For zinc, the pattern is reversed. Urban areas have higher ratios in the fall and winter than in spring and summer, and show little differences for copper by season.

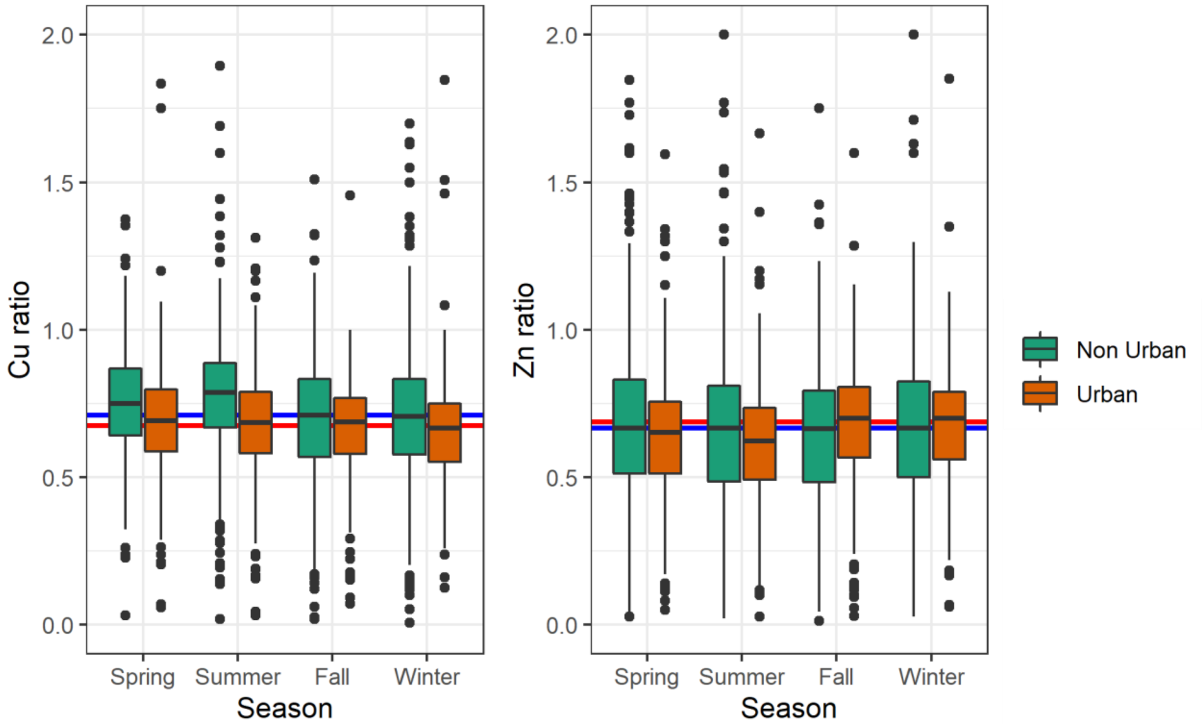

Figure 3-16: Boxplot of metal ratio by season at AC SoE sites. Data from 2003 to 2021, depending on site (see Appendix A). The red line is the default setting used in the FWMT and the blue line the sample median (excluding those that were censored for both total and dissolved metal)

There is considerable variation in metal ratios over time, with a general trend of increasing metal ratios over time as illustrated by the pair plots (section 3.2.3, Figure 3-10 and Figure 3-11). A linear mixed model was fitted to the data, assuming a random intercept (see Figure 3-17). The overall trend explains 9.5% of the observed variance in the whole copper ratio dataset, increasing to 10.3% when including seasonality. A smaller fraction of the zinc ratio variability is explained by time. For the log-transformed ratios, 3.7% of the observed variability was explained by time, slightly increasing to 3.8% when including seasonality.

A possible reason for the trend over time could be changing stream monitoring sites. Before 2010, most of the monitored sites were urban. After 2010, more non-urban sites were monitored, with further non-urban sites added after 2018 (shown by more green dots after 2010 in Figure 3-17). The effect of adding new sites was investigated using a LMM and assuming random slopes and intercepts. The results suggest sample site and date are the most important factors. The overall variance in the copper ratio explained in this analysis increases to 13.7% and 15.6% when seasonality was included.

Besides the addition of new sites, caution also needs to be exercised when interpreting this data because of censoring. Due to changing detection limits, a higher proportion of the pre-2010 observations were censored compared to the post-2010 observations, and we do not have a good approach for dealing with censored ratio data.

In summary, there is a trend of increasing metal ratios over time, and seasonality and changes in sampling sites can only explain some of the observed variation in the monitoring data. Other potential explanations not explored here could be urbanisation or changes in traffic.

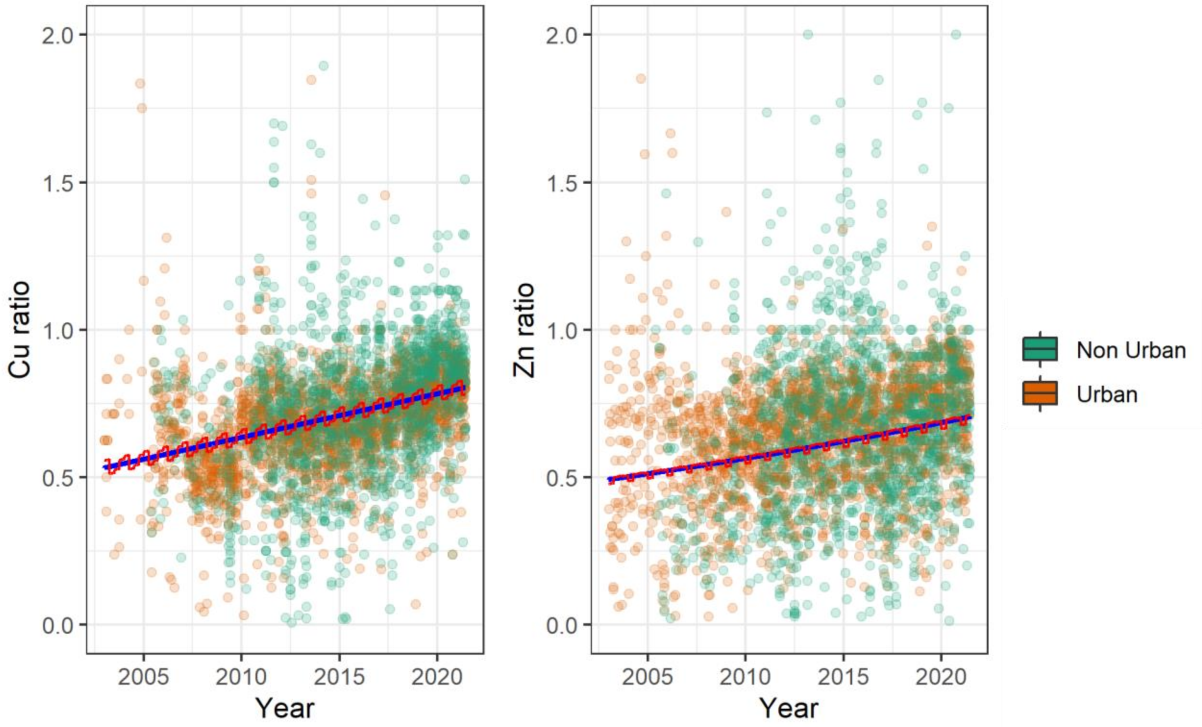

Figure 3-17: Plots of metal ratio over time based on AC SoE sites. Data from 2003 to 2021, depending on site (see Appendix A). The blue line is the trend, and the red line trend plus seasonality. Lines fit using linear mixed model assuming random intercept for sample site.

3.2.7 Variation by TSS

Figure 3-10 and Figure 3-11 above highlighted a negative correlation between metal ratios and TSS. Taking a closer look at the data (Figure 3-18), there is a negative association between metal ratios and TSS, as illustrated by the green (non-urban) and dark orange (urban) regression lines. The two regression lines on each graph showed similarities, suggesting the catchment land use did not have a great impact on the average relationship between metals and TSS. However, there was substantial variation around the regression lines. The copper regression lines explained (r^2) 11.5%, and the zinc line 18.9% of the observed variation.

Consideration was given to whether the results may have been impacted by censoring of the metal ratio. Although there are several censored values in the dataset, the censored values appeared to be fairly evenly spread (not shown on this plot), suggesting censored values do not influence the bivariate relationship between metal ratios and TSS.

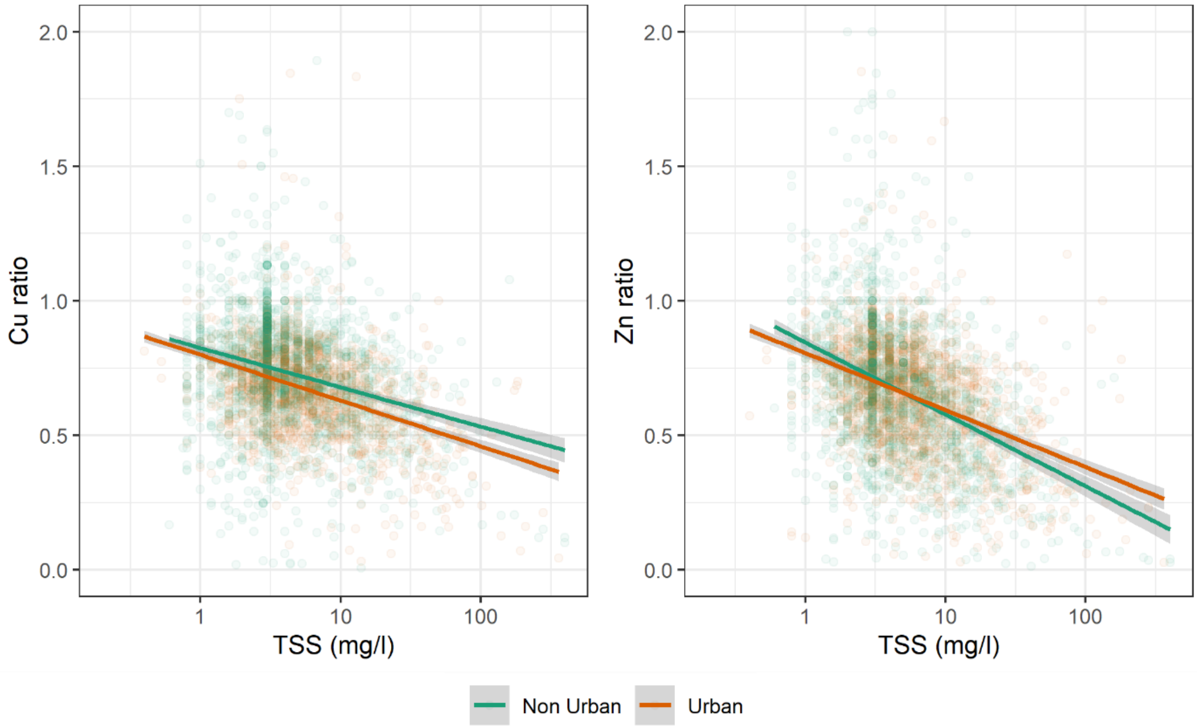

Figure 3-18: Scatter plots of metal ratio and TSS based on AC SoE observations. Data from 2003 to 2021, depending on site (see Appendix A). The green line is a best fit line for non-urban and dark orange for urban, showing a trend of decreasing ratio (lower dissolved metal) with increasing TSS for both copper and zinc for urban and non-urban observations.

Studies reported in the literature suggest an inverse relationship between metal partitioning and TSS (Baum et al. 2021, Lu & Allen 2006, Prestes et al. 2006). These studies reported the partitioning coefficient (K_d) rather than the metal ratio considered in this work. The partitioning coefficient is the mass of metal sorbed onto particles (TSS) divided by the dissolved concentration. The K_d values were estimated for the SoE monitoring data. They did indeed show a negative relationship between the partitioning coefficient and TSS.

In summary, higher TSS is associated with lower metal ratios for both copper and zinc. Land use does not change this pattern.

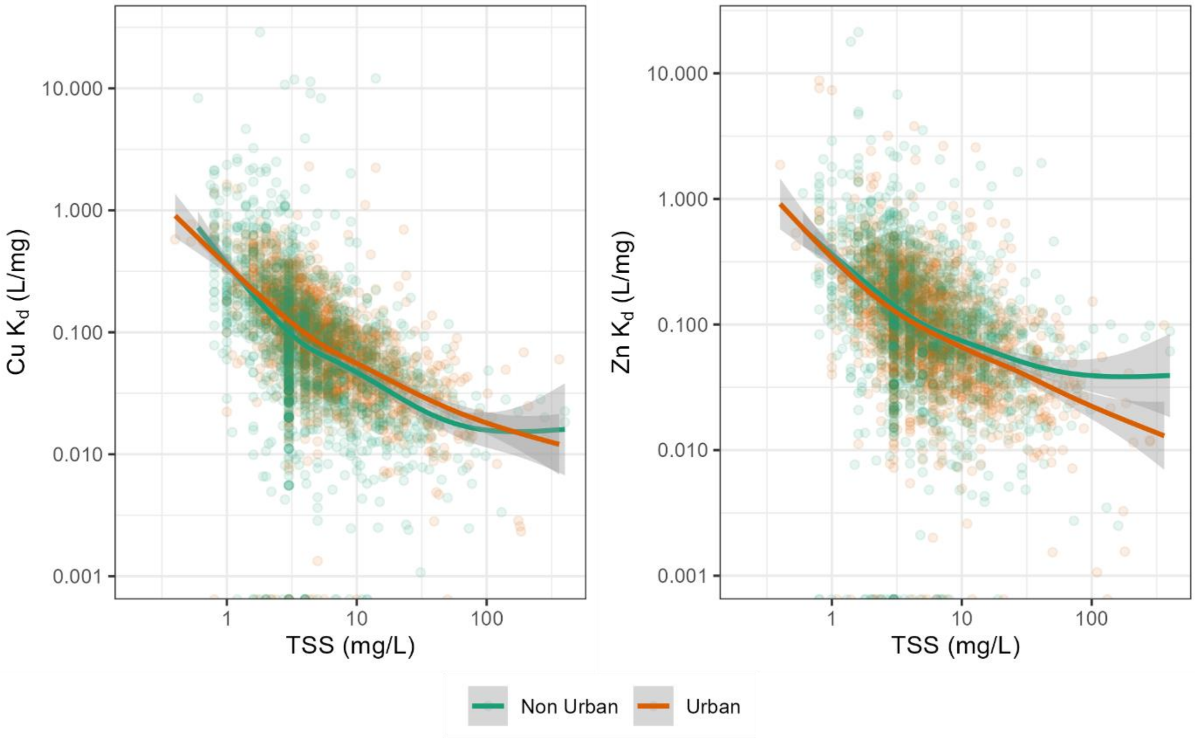

Figure 3-19: Partitioning coefficient and TSS based on AC SoE observations . Data from 2003 to 2021, depending on site (see Appendix A). The lines are best-fit curves for urban and non-urban sites. The two curves are similar for both copper and zinc, suggesting that land use does not strongly influence the coefficient.

3.2.8 Variation by total metal

Figure 3-10 and Figure 3-11 above highlighted a negative correlation between metal ratios and total metal concentration, at least for copper. The relationship between the ratios and total metals are explored further in Figure 3-20. It is clear for both copper and zinc that there is a tendency for urban samples to have higher concentrations of total metals than the non-urban sites. The copper ratio decreases with increasing total copper similarly for urban and non-urban samples. There is a different picture for zinc. In urban samples, the zinc ratio shows a slight increase with total zinc, whilst in non-urban the ratio decreases. But it should be noted that the non-urban zinc samples may be influenced by censoring. The two distinct curves of green squares are made up of censored data points.

In summary, higher total copper is associated with lower copper ratios. There is not as clear a picture for zinc.

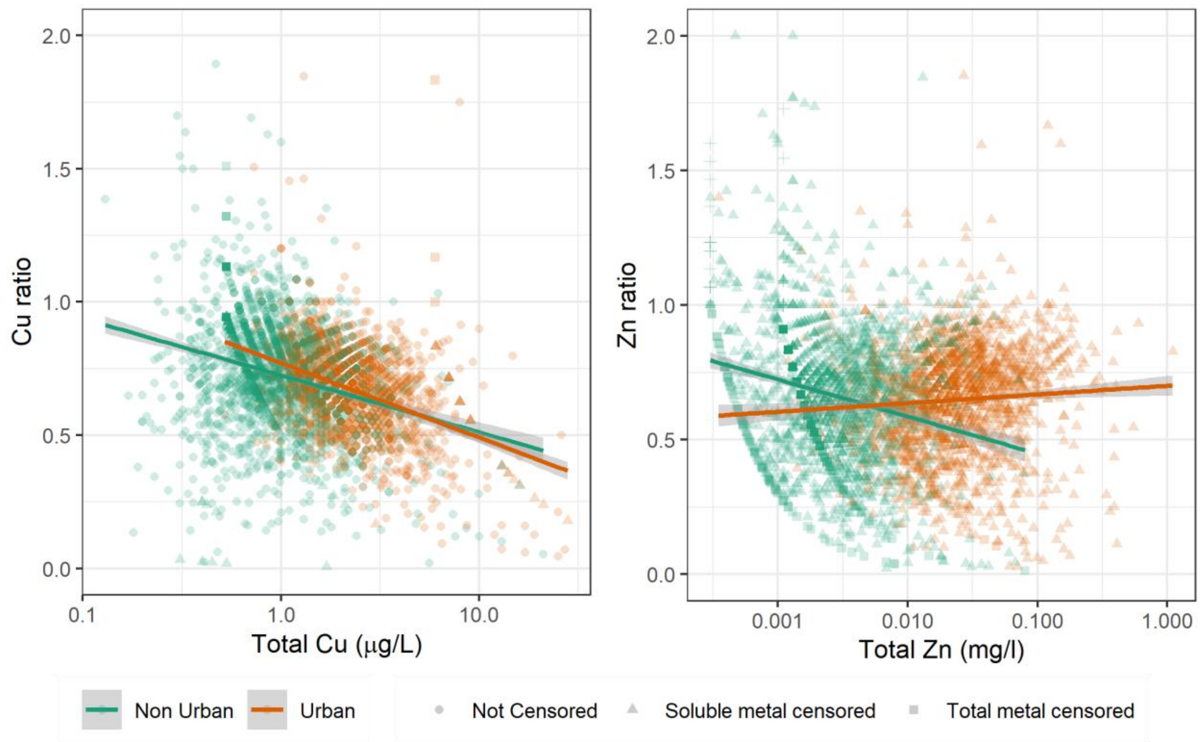

Figure 3-20: Scatter plots of metal ratio and total metals based on AC SoE observations. Data from 2003 to 2021, depending on site (see Appendix A). Lines are linear regressions/ best fit lines.

3.2.9 Statistical modelling

Although the EDA results presented above give insights into the factors affecting metal ratios, it does not help us estimate what metal ratios would be under various circumstances, neither does is help us understand how the various attributes interact. Therefore, regression was used to predict and provide further insights into the behaviour of metal ratios. We applied two regression approaches: multiple linear regression (MLR) and Random Forests (RF).

Three MLR and RF models were developed for the copper and zinc ratios (called: Time, DNPOC, and flow). As some data items are missing, each model was presented with a different subset of complete predictors. For example, monitoring for DNPOC has only recently started, and flow measurements are not available for all sites. The best subset procedure was run to further subset the predictors to choose the optimal MLR model (James et al. 2021). The resulting MLR models are shown in Table 3-4 and Table 3-6 and the predictor attributes offered to each model as well as the performance of the MLR and RF models are shown in Table 3-5 and Table 3-7. Note that is is not possible to write down a simple equation for a RF model unlike MLR models.

Modelling copper

The three MLR models explained approximately a quarter of the observed variance in the dataset. In contrast, the RF model explained about a third of the variance (Table 3-5). The models suggests that the copper ratio decreases (less dissolved copper) as TSS, total copper, and temperature increase (Table 3-4). On the other hand, the average copper ratio goes up (more dissolved copper) over time, DNPOC, land use and flow.

Table 3-4: MLR models for copper ratio. Each model was presented with a different subset of predictors (attributes) and through a process of best subset selection, the optimal model was chosen. Model no. refers to model name in Table 3-5.

Equation	Model no.
$Cu\ ratio = 0.158 - 0.101log_{10}(TSS) + 0.016Year + 0.048land_{Urban} - 0.136log_{10}(Cu\ total) + \epsilon$	1
$Cu\ ratio = -0.105 - 0.104log_{10}(TSS) + 0.067land_{Urban} - 0.311log_{10}(Cu\ total) + 0.204log_{10}(DNPOC) - 0.005Temp + \epsilon$	2
$Cu\ ratio = 0.008 - 0.110log_{10}(TSS) + 0.012Year + 0.058land_{Urban} - 0.272log_{10}(Cu\ total) + 0.204log_{10}(NormalisedFlow) + \epsilon$	3

ϵ is error.
Year is time measured in years starting from 2003
Land is classified as either urban(1) or non-urban(0)

Higher copper ratios with increasing flows and urban land use appears counter-intuitive, especially in light of the EDA results above. However, these variables are not independent - urban sites tend to have higher metal concentrations as shown in Figure 3-20. In addition, TSS and flow are related as shown in Figure 3-10, so if all other things were kept equal, urban areas would have lower ratios (less dissolved copper) than non-urban areas. In practice, this does not happen.

It is interesting to see the relationship between organic carbon and metal ratio. Heier et al. (2010) and Lu and Allen (2006) noted that organic carbon plays an important role in the concentration and partitioning of copper in water.

Table 3-5: Attributes offered to Copper ratio MLR and RF models and model performance. Note: year zero equals 2003 for this model.

Predictors	Time model - 1	DNPOC model - 2	Flow model - 3
(Intercept)	Used	Used	Used
log10(TSS)	Used	Used	Used
Time (Years)	Used	Not used	Used
Land use (Urban = 1, non-urban = 0)	Used	Used	Used
log10(Cu total)	Used	Used	Used
log10(DNPOC)	Not offered-	Used	Not offered
Temperature	Not used	Used	Not used
log10(Normalised flow)	Not offered	Not offered	Used
log10(Conductivity - field)	Not used	Not used	Not used
pH – field	Not used	Not used	Not used
Performance criteria			
r^2 MLR	0.267	0.242	0.243
r^2 random forest	0.358	0.330	0.374
Number of observations in test set	1138	683	356

Note: for this model, year zero equals 2003.
"Used" means this predictor was used in the MLR model
"Not used" measn the predictor was offered to the model but the the Best subset preocedure dis not select it
"Not offered" measn this preidictor was not offered to the MLR or RF model

It is possible to estimate the relative importance of variables in a RF model. A RF model was applied to a dataset with 12 predictor variables (including some not used in the MLR modelling) and 268 complete observations. In order of decreasing importance, the key variables were: total copper, TSS, total zinc, DNPOC, normalised flow, year, electrical conductivity (field), total hardness, pH (field), total alkalinity, water temperature, and land use. This ranking supports the MLR findings above. It also suggested that excluding total alkalinity and hardness, due to a limited number of measurements, has probably not adversely affected our understanding of copper partitioning.

Modelling zinc

The MLR models (Table 3-6) explained about a quarter of the observed variance in the log-transformed zinc ratio in the test datasets (r^2 values in Table 3-7). The log transformation was applied as it produced better predictions than using the untransformed data. The random forest model explained a quarter to a half of the variance. However, caution needs to be exercised when suggesting one model is better than the other. The relative performance might change if different training and test sets were chosen.

The models suggest that the zinc ratio decreases (less dissolved zinc) as TSS, total zinc, pH, flow and temperature increase. The zinc ratio goes up with land use. The ratio also goes up with year in the time and flow models, but the opposite trend is noted for the DNPOC model (see Table 3-6). Note that although referred to here as the DNPOC model, DNPOC was not selected by the best subset procedure as being important for zinc ratio. On the other hand pH was selected as important, contrasting with the copper models.

A random forest model was applied to a dataset with 12 predictors and 268 observations. In order of decreasing importance, the key variables were: total zinc, normalised flow, pH(field), year, total copper, water temperature, total alkalinity, DNPOC, electrical conductivity (field), total hardness, and land use. It is interesting to note that copper concentrations can be used to predict zinc partitioning. This is probably due to common causes behind the generation of both metals, such as urbanisation.

Table 3-6: MLR models for zinc ratio. Each model was presented with a different subset of predictors (attributes) and through a process of best subset selection, the optimal model was chosen. Model no. refers to model name in Table 3-7.

Equation	Model no.
$log_{10}(Zn\ ratio) = 0.297 - 0.191 log_{10}(TSS) + 0.008 Year + 0.120 land_{Urban} - 0.075 log_{10}(Zn\ total) - 0.006 Temp + \epsilon$	4
$log_{10}(Zn\ ratio) = 0.684 - 0.225 log_{10}(TSS) - 0.014 Year + 0.122 land_{Urban} - 0.082 log_{10}(Zn\ total) - 0.082 pH + \epsilon$	5
$log_{10}(Zn\ ratio) = 0.008 - 0.237 log_{10}(TSS) + 0.004 Year + 0.037 land_{Urban} + 0.043 log_{10}(NormalisedFlow) + \epsilon$	6

ϵ is error.
Year is time measured in years starting from 2003
Land is classified as either urban(1) or non-urban(0)

In summary, both copper and zinc ratios are sensitive to TSS and the concentration of their respective total metals. Urbanisation results in higher metal concentrations, and flow plays a major part in determining TSS in streams. The MLR modelling suggests some possibly surprising results, with metal ratios going up in response to increased flow and higher ratios in urban areas. Though these results may appear counter-intuitive, they are based on the assumption that all other factors are held constant, which does not happen in practice.

Table 3-7: Attributes offered to the zinc ratio MLR and RF models and model performance. Note year zero equals 2003 for this model.

Predictors	Time model - 4	DNPOC model - 5	Flow model - 6
log_{10}(TSS)	Used	Used	Used
Time(Years)	Used	Used	Used
Land use (Urban = 1, non-urban = 0)	Used	Used	Used
log_{10}(Zn total)	Used	Used	Not used
pH (field)	Used	Used	Not used
Temperature	Used	Used	Not Used
log_{10}(DNPOC)	Not offered	Not used	Not offered-
log_{10}(Normalised flow)	Not offered	Not offered	Used
log10(Conductivity - field)	Not used	Not used	Not used
Performance criteria			
r^2 MLR	0.220	0.237	0.273
r^2 MLR (random forest)	0.340	0.477	0.248
Number of observations in test set	1334	473	353

Note: for this model, year zero equals 2003.
"Used" means this predictor was used in the MLR model
"Not used" means the predictor was offered to the model but the the best subset procedure did not select it
"Not offered" means this prediictor was not offered to the MLR or RF model

3.3 Comparing stream and stormwater

This section compares urban and non-urban streams and stormwater in terms of total and dissolved metals, metal ratios and TSS, the key variables identified above. Stormwater is a significant source of metals in urban streams.

Higher concentrations of total metals are associated with higher concentration of dissolved metals, with stormwater samples having the highest total and dissolved metal concentrations, and non-urban samples the lowest (Figure 3-21). The red line in the charts represents the FWMT default value. The line broadly goes through the middle of the urban and non-urban SoE monitoring, but not the stormwater samples. There is also a greater variation in dissolved metals relative to total metals for the stormwater samples than for the SoE stream samples.

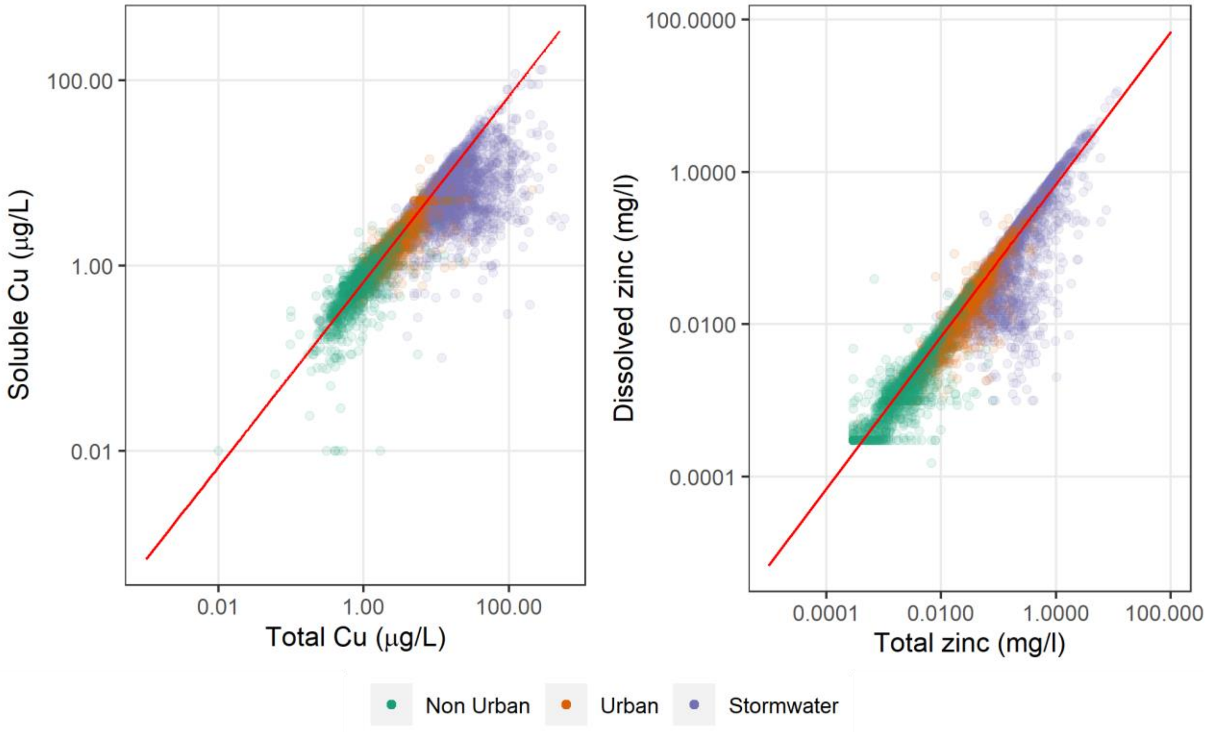

Figure 3-21: Scatter plot of total and dissolved metal in stream and stormwater. Stormwater data are the untreated stormwater from URQIS supplemented with additional stormwater studies as described in section 2.2.1 (2001 -2021); non-urban and urban data are the stream data from Auckland Council SoE monitoring (2003- 2021). The red line is the default ratio used in FWMT.

Stormwater (purple box) in Figure 3-22 and Figure 3-23 has greater variation in metal ratios than stream water. In addition, the stormwater samples have the lowest copper and zinc ratios (lower dissolved metals, higher particulate), and non-urban stream sites have the highest. The mean (median) copper ratios are 0.775 (0.764), 0.681 (0.690) and 0.432 (0.408) for non-urban, urban and stormwater samples, and for zinc they are 0.755 (0.727), 0.652 (0.667) and 0.581 (0.631) respectively. Though there are differences in the means and medians, there is overlap between the urban and non-urban metal ratios for both metals, and also overlaps with the zinc stormwater ratio, but not copper (i.e., stormwater copper ratios are notably lower than either urban or non-urban ratios, whereas all three share broadly overlapping zinc ratios).

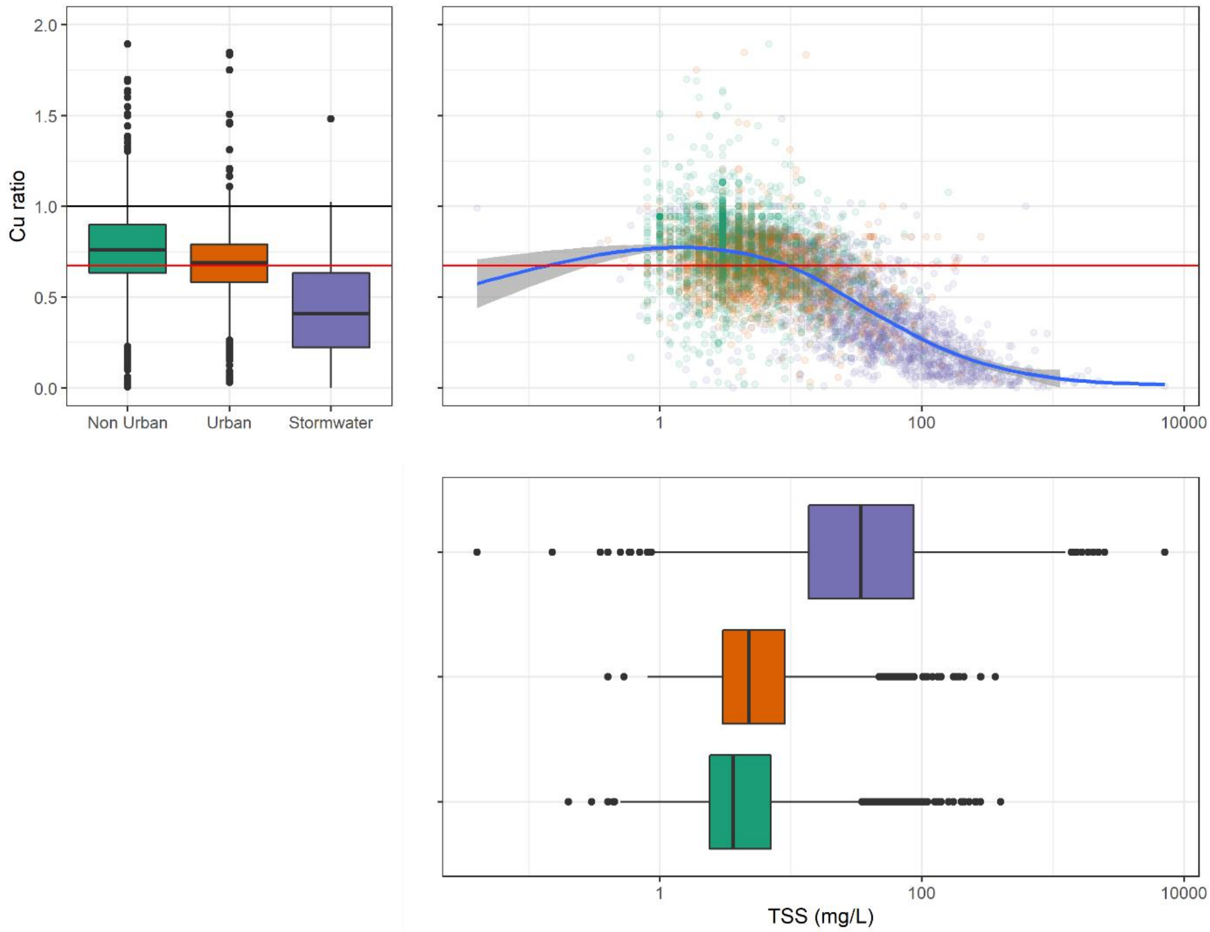

Figure 3-22: Copper ratio and TSS for stormwater and streams. Stormwater data are the untreated stormwater from URQIS supplemented with additional stormwater studies as described in section 2.2.1 (2001 - 2021); non-urban and urban data are the stream data from Auckland Council SoE monitoring (2003- 2021). The blue line is a best fit line, and the red line is the default value used in the FWMT.

As well as there being differences in metal ratios, there are differences in TSS between the three groupings. Stormwater typically has much higher TSS than stream water. On average, the urban sites had higher TSS than non-urban sites, but there was substantial overlap.

Unpacking the relationship between metal ratios and TSS requires us to understand the differences in dissolved, particulate and total metal behaviour with respect to TSS. Generally, metal concentrations increase with increasing TSS (Figure 3-24), with the exception of dissolved metals in stormwater. The dissolved zinc concentrations go down, but dissolved copper changes very little with increasing TSS. Further, though metal concentrations in streams increase with TSS, there are slightly different trends for the urban and non-urban data. The urban trend appears to be a mixture of stormwater and non-urban trends rather than a simple continuation of the non-urban trend with higher TSS. This observation makes sense, as stormwater is one of the main sources of metals in urban streams (Muller et al. 2020).

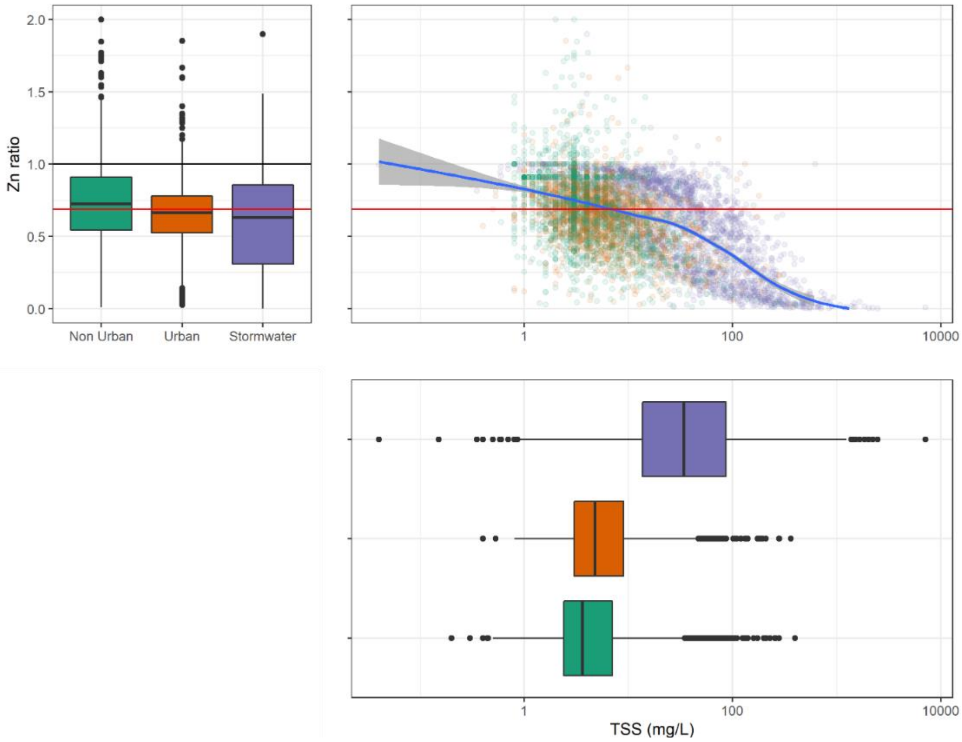

Figure 3-23: Zinc ratio and TSS for stormwater and streams. Stormwater data are the untreated stormwater from URQIS supplemented with additional stormwater studies as described in section 2.2.1 (2001 - 2021); non-urban and urban data are the stream data from Auckland Council SoE monitoring (2003- 2021). The blue line is a best fit line, and the red line is the FWMT default value.

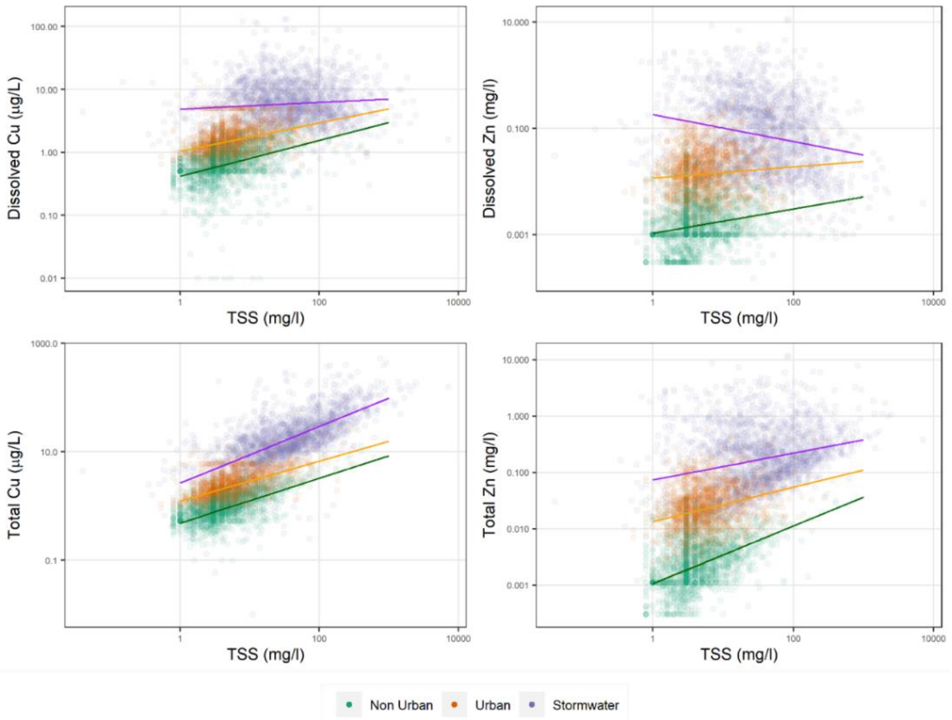

Figure 3-24: Variation in total and dissolved copper and zinc for stream and stormwater relative to TSS. Stormwater data are the untreated stormwater from URQIS supplemented with additional stormwater studies as described in section 2.2.1 (2001 -2021); non-urban and urban data are the stream data from Auckland Council SoE monitoring (2003- 2021). The green line is the best fit for non-urban streams, orange for urban streams, and purple for stormwater.

4 Implications for FWMT modelling

This section summarises the findings and discusses them in the context of the current FWMT modelling approach. It goes on to make recommendations to improve future iterations of the FWMT.

4.1 Summary of findings and discussion

The objective of this study was to analyse the observed metal partitioning in stormwater and streams, and identify factors that could explain the observed variation in the partitioning of copper and zinc. The analysis was to consider factors such as flow, concentrations of metal and differences between watersheds, and compare them with the partitioning used in the FWMT.

There were distinct differences in the total and dissolved metal concentration between stormwater, urban and non-urban (rural & lifestyle, reference, and exotic forests) streams, with stormwater having the highest concentrations, and non-urban streams the lowest. The difference in metal ratios between these sites was not so clear-cut and varied spatially and over time.

This study found variations in the observed metal ratios in stormwater and streams. In most cases, the interquartile range of the copper ratio (25 out of 34 streams) and the zinc ratio (29 out of 34 streams) included the FWMT default value of 0.676 for copper and 0.688 for zinc (i.e., the additional sites and records since 2017 did not alter the regional median metal ratios substantially). There were examples of streams with average ratios both above the default values and below. In the case of stormwater, a slightly different picture emerged. In all “land use” cases the median observed copper ratios were lower than the default value (meaning more is in particulate form). The exception was the car park dataset, where the median value was close to the default. In the case of zinc, roads and residential land use had lower rates than the default, whereas car parks, CBDs, industry and roofs all had higher median ratios (meaning more in dissolved form).

Non-urban sites had the highest metal ratios (a high fraction of metals being in a dissolved form), and stormwater had the lowest. The variation between and within streams is best explained by TSS and the total level of metals. The more TSS in the water column, the greater the proportion of total metal attached to particles. Higher concentrations of total metals tend to occur in urban areas and may suggest stormwater input. However, the total metal concentrations are not constant, and total metal concentrations tend to be higher when TSS is high, due to high flow. Overall, higher levels of TSS and total metals tend to reduce metal ratios in streams, as illustrated conceptually in Figure 4-1.

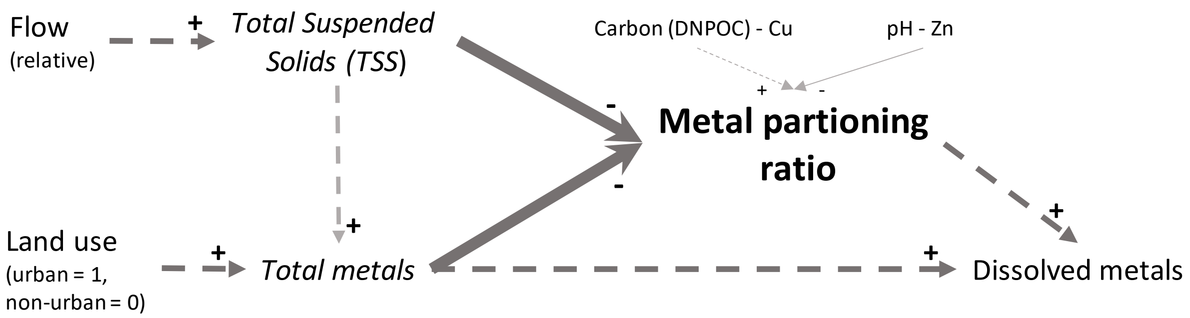

Figure 4-1: Conceptual model of metal partitioning in streams. The line weight reflects the strength of the relationship. Dashed lines show a positive relationship between the variables (so when the flow goes up, TSS goes up), and solid lines show an inverse relationship (TSS goes up, Metal partitioning ratio goes down).

Both flow and land use can be used to estimate metal ratios. There is a tendency for ratios to go down when flow goes up, but the opposite is true when we control for such things as TSS and total metals. Streams in urban dominated catchments have lower ratios than non-urban, but higher when controlling for TSS and total metals. These counter-intuitive results can be explained by the fact that flow and land use both play an important part in determining the amount of metal and TSS in streams. Other important factors are DNPOC for copper and pH for zinc. Higher concentrations of organic matter (DNPOC) increase copper ratios (more in dissolved form), and lower pH (more acidic) increases zinc ratios.

Overall, we explained a quarter to almost a half of the observed variation in metal ratios. The concentration of metals is relatively low, particularly for non-urban streams, compared to detection limits. The errors in the estimated copper ratios could be in the order of ±90% of the estimated value. This means that there is a high noise to signal ratio in the data. We will never be able to predict the observed metal ratios perfectly, however, using monitoring with lower detection limits than those reported, such as ultatrace methods could help increase accuracy.

The SoE monitoring is based on monthly samples. However, the analysis and evidence from the literature suggest that higher levels of metals and lower metal ratios occur during events that generate stormwater and higher levels of sediment (TSS). To get a better handle on metal ratios (and total metals), high-frequency sampling during storm and high flow events will provide far greater insight into the dynamics of these metals than monthly sampling alone. This finding is important in the context of the FWMT, a continuous model, wheremetals are predicted during high flow events, which are likely to have higher metal concentrations. In contrast monthly SoE sampling is somewhat biased to baseflow conditions ().

The FWMT Peer Review Team identified that it would be useful to better understand the variability of dissolved particulate ratios under different flow regimes and catchments. Our analysis has demonstrated that there *is* evidence of partitioning being a function of flow, primarily mediated through TSS or particulate matter. Though there was some evidence that streams in urban catchments have a lower copper ratio than a stream in catchments with other land use, catchment land use does not directly explain the observed variation. However, this does not mean that land use is irrelevant to the copper and zinc ratio. It simply means that the observed variation in the metal partition ratio cannot be explained by land use in isolation from the impact urban land use has on flow, TSS and the amount of metals entering streams.

The current FWMT model estimates the dissolved metal concentration by first estimating the concentration of total metals, and then applying a partitioning parameter (0.676 for copper and 0.688 for zinc). Based on the analysis of SoE data, these parameters are the correct order of magnitude, however, they do not take into account that these ratios do change in response to flow and water quality parameters such as TSS. Both median and 95th percentile statistics are used for grading the state of streams against metal attribute tables. As 95th percentile metal concentrations are frequently associated with higher flows, use of the median partitioning parameter may over-estimate the dissolved metal concentration. Therefore, the model predictions, and the grading of metals,could be improved by incorporating the findings from this report.

It should be noted that the variation in the metal ratios is much smaller than the observed variation in the total metals - the coefficients of variation are approximately 0.5 and 2.0, respectively. This suggests that dissolved metal ratios may be far more sensitive to the estimated level of total metals than the partitioning parameter, and therefore model improvements that decrease the uncertainty in total metal predictions would be equally or more beneficial to improving the accuracy in metal grading.

4.2 Recommendations

Based on the discussion above, there are three recommendations to come out of this report

1. Given the FWMT models flow, TSS and total metals, consideration should be given to using the findings of this report to improve the estimate of dissolved metals in future iterations of the model.

2. The measured concentration of metals is quite low relative to the limit of detection, particularly in non-urban streams. This means that there is a high level of uncertainty in the estimation of partitioning ratios. Consideration should be given to using methods with lower limits of detection. This would reduce error and allow us to untangle the more subtle factors which control metal partitioning.

3. We recommend the use of high-frequency sampling. This sampling should target before, during and after high flow events, including events that generate storm flows. This recommendation is made because these events create higher concentrations of metals, and the current monthly monitoring program does not adequately capture how metals and metal partitioning change over these events.

5 Acknowledgements

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Appendix A Dates monitoring began at SOE sites

Table A-1: List of SOE monitoring sites for which water quality data was used in this report. Dominant land use from Buckthought et al. (2020).

			Date regular monitoring began for:		
Stream reporting name	**Station number**	**Dominant land use**	**Metals**	**TSS**	**DOC, hardness**
Matakana River	6604	Rural & lifestyle	Aug-2010	1986	Nov-2017
Kaukapakapa River	45415	Rural & lifestyle	Jun-2018	2009	Nov-2017
Kumeu River	45313	Rural & lifestyle	Aug-2010	1993	Nov-2017
Makarau River	45505	Rural & lifestyle	Aug-2010	2009	Nov-2017
Riverhead Stream	45373	Exotic	Aug-2010	2009	Nov-2017
Cascades Stream (Waitakere)	44603	Reference	Aug-2010	1986	Nov-2017
Mahurangi River (Forestry)	6811	Exotic	Aug-2010	1993	Nov-2017
Mahurangi River (Warkworth)	6804	Rural & lifestyle	Aug-2010	1993	Nov-2017
Nukumea Stream	7171	Reference	Jan-2012	2012	Nov-2017
Okura Creek	7502	Rural & lifestyle	Jun-2005	2003	Nov-2017
Vaughan Stream	7506	Urban	Jun-2005	2001	Nov-2017
Waiwera Stream	7104	Rural & lifestyle	Aug-2010	1986	Nov-2017
West Hoe Stream	7206	Reference	Jun-2018	2002	Nov-2017
Avondale Stream	8019	Urban	Jan-2012	2012	Nov-2017
Lucas Creek	7830	Urban	Jan-2003	1993	Nov-2017
Oakley Creek	8110	Urban	Jan-2003	1994	Nov-2017
Opanuku Stream	7904	Reference	Jun-2018	1986	Nov-2017
Oteha Stream	7811	Urban	Jan-2003	1986	Nov-2017
Rangitopuni River	7805	Rural & lifestyle	Jun-2018	1986	Nov-2017
Cascades Stream (Waiheke)	74701	Rural & lifestyle	Jun-2018	2013	Nov-2017
Onetangi Stream	74401	Reference	Jun-2018	2013	Nov-2017
Omaru Creek	8249	Urban	Jan-2009	2009	Nov-2017
Otara Creek (South)	8214	Urban	Sep-2007	1985	Nov-2017
Otara Creek (East)	8205	Urban	Jul-2005	1992	Nov-2017
Botany Creek	8217	Urban	Sep-2007	1992	Nov-2017
Pakuranga Creek	8215	Urban	Sep-2007	1992	Nov-2017
Ngakoroa Stream	43829	Rural & lifestyle	Jun-2018	1993	Nov-2017
Papakura Stream (Upper)	1043837	Rural & lifestyle	Jan-2012	2012	Nov-2017
Papakura Stream (Lower)	43856	Rural & lifestyle	Sep-2010	1993	Nov-2017
Puhinui Stream	43807	Urban	Jan-2003	1994	Nov-2017
Waitangi Stream	43601	Rural & lifestyle	Jun-2018	2009	Nov-2017
Whangamaire Stream	438100	Rural & lifestyle	Jun-2018	2009	Nov-2017
Wairoa River	8516	Rural & lifestyle	Sep-2010	1986	Nov-2017
Wairoa Tributary	8568	Reference	Jun-2018	2009	Nov-2017