Developing Auckland-Specific Ecosystem Health Attributes for Copper and Zinc: Summary of work to date and identification of future tasks

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RIMU Research and Evaluation Unit

Auckland Council
Te Kaunihera o Tāmaki Makaurau

Developing Auckland-specific ecosystem health attributes for copper and zinc: summary of work to date and identification of future tasks

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Cover photograph of Oakley Creek waterfall Auckland, by Luke Harvey

Preface

The National Policy Statement for Freshwater Management 2014 (NPS-FM) has compulsory water quality attributes within the National Objectives Framework (NOF). Auckland Council identified that these attributes did not sufficiently address urban water quality issues and determined that Auckland-specific urban water quality attributes should be developed. This approach was endorsed by the Ministry for the Environment. A workshop was held in 2014 with Auckland Council staff from the Research, Investigations and Monitoring Unit (RIMU, now the Research and Evaluation Unit) and the Stormwater Unit (now the Healthy Waters Department) and research providers. Greater Wellington Regional Council and Environment Canterbury staff also attended, due to potential for the work to be used for attribute development for urban centres nation-wide. At this workshop, a “strawman” attribute table was developed, for discussion and refinement over the course of the project.

Following the workshop, there was analysis of the copper and zinc data collected by Auckland Council and investigations of other data and information as required for development of attributes. The bulk of this work was undertaken in 2015 with the findings reported to Auckland Council in a working paper (Williamson et al. 2015) but not formally reported (i.e., in a technical publication) at that time as further work was required. Further analyses of metal concentrations and flow were subsequently undertaken in 2016/2017 and not formally reported. Both phases of work identified further tasks to be undertaken and neither developed a final attribute table.

Although this work remains incomplete, Auckland Council recognises a need for the work undertaken to date to be publicly available. This will enable other organisations (other councils, government agencies) to use the analyses undertaken and information compiled and proceed with the tasks identified as required for attribute development. This discussion paper therefore incorporates the analyses from the two phases of work, and outlines the further tasks required to develop copper and zinc attributes.

Executive summary

Copper and zinc concentrations in Auckland urban streams indicate they may be contributors to degraded ecological health (Mills & Williamson 2008) but these are not currently included as attributes in the National Objectives Framework (NOF) of the National Policy Statement for Freshwater Management 2014 (NPS-FM). This discussion paper summarises work undertaken towards developing copper (Cu) and zinc (Zn) as Auckland-specific freshwater attributes for ecosystem health. Although the work is incomplete, Auckland Council recognises a need for the work undertaken to be publicly available to enable other organisations to use the information and proceed with the tasks identified as required for attribute development. This discussion paper therefore incorporates the analyses from the two phases of work, and outlines the further tasks required to develop copper and zinc attributes.

The scope of the project included:

- Recommendations on how best to integrate copper and zinc into the format of an ecosystem health attribute table for the Auckland region in alignment with the NOF framework (i.e., for incorporation into NPS-FM implementation).
- Understanding what is required to provide scientific robustness and technical defensibility to attribute tables for Cu and Zn including bioavailability aspects and identification of significant implementation and management considerations.
- Outlining subsequent work required for completion of attribute tables.

The paper summarises the ANZECC and USEPA guidelines which could be used to provide numerical objectives in an attribute table. It recommends using revised the ANZECC guidelines in line with an expanded toxicity database and the new ANZECC guidance for chronic definitions, endpoints, statistical fitting, and toxicity modifying factors used to adjust guideline values.

The ANZECC guidelines provide a decision tree approach and guidelines that can be adjusted for site-specific water chemistry to account for varying bioavailability. This requires knowledge of the water chemistry, and consideration of whether to use values from baseflow or storm flows. A more complex alternative is highlighted, that bioavailability could be incorporated by modelling speciation, using either a biotic ligand model, a simplified model based on the biotic ligand model, or an alternative chemical speciation model.

Attribute tables require sample statistics, which compare monitoring data to numerical objectives. Previous NOF attribute tables have used two statistics, representing a median and a ‘maximum’ to protect from both chronic and acute effects. The median represents the value below which 50 per cent of observations may be found and generally reflects the average and baseflow flow conditions – and represents chronic exposure. The maximum condition can be defined as maximum or 95th percentile or other percentiles and can be used to protect from acute exposures.

The ANZECC (2000) guidelines and US EPA acute criteria were used in strawman tables in this report using differing levels of protection (e.g., 99% protection) for different band thresholds. When summary statistics for Auckland streams (data from 2005 to 2014) was compared to such tables, the urban streams achieved attribute gradings of C or D.

The report explores Auckland freshwater stream data from Auckland Council state of the environment monitoring sites (1995 to 2014) complemented by a catchment study in the Twin Streams, Waitākere catchment (2003-2006). The data exploration includes analysis of land use effects, dissolved/total metals relationships and temporal trends. The analysis showed that the ANZECC (2000) guidelines for both Cu and Zn were exceeded in many urban streams and at times the US EPA acute criterion for zinc was also exceeded. Guidelines were only occasionally exceeded in rural and forested streams, indicating that Cu and Zn management is predominantly an urban issue in Auckland. The absence of strong decreasing trends in Cu and Zn concentrations indicates that management will be required into the future.

The stream data was also used to examine relationships between concentration and flow. There is evidence from numerous data sets that in-stream concentrations of Cu and Zn are higher during storm events than during baseflow. However, statistical relationships between concentration and flow were only weak (albeit there were only four sites where the analysis was possible), potentially due to first-flush effects and hysteresis common to urban streams.

The discussion paper identifies a number of further tasks that are required to develop attribute tables:

1. Replace ANZECC (2000) chronic guidelines in the strawman table with revised ANZ water quality guidelines.
2. If acute ANZECC guidelines or New Zealand-specific acute thresholds are developed, these could be used for thresholds in preference to US EPA Criterion Maximum Concentration (CMC) values.
3. Assess whether to incorporate speciation and bioavailability of Cu and Zn, through either use of look-up tables and equations to adjust threshold values; or using a Biotic Ligand Model (BLM) or simplified BLM tool to estimate bioavailable concentrations to compare to values in the attribute table; or developing a tool that provides band thresholds based on local water chemistry.
4. Investigate the concentrations during high flows in urban streams and their importance, by:
    - Collating and analysing existing data on dissolved Cu and Zn concentrations over full storm event hydrographs, to define the first flush effect, and the length of time organisms are exposed to higher storm-associated concentrations.
    - Assess whether storm-related exposures are likely to cause acute toxicity, based on observed duration and in reference to New Zealand and international literature for tests of acute exposures (short-term) and pulsed exposures (repetitive short-term exposures).
5. Investigate the implications of using a maximum sample statistic compared to a 95th percentile, including whether ongoing monitoring programmes are able to accurately determine a maximum (i.e., whether sampling is biased to lesser flow conditions and/or too

infrequent to resolve maxima) and the implications of the permissible exceedances if percentiles are used.

6. Assess the implications of the final attribute table for integrating freshwater with coastal management (e.g., estuarine management outcomes, including sediment quality).

There are also a number of tasks that should be undertaken by Auckland Council to assess whether the current monitoring programme (monthly monitoring of streams regardless of flow) is sufficient to assess compliance with any attribute tables once developed.

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Abbreviations

Abbreviation	Definition: (relevant environment)
ACR	Acute to chronic ratio
ANZECC	Australian and New Zealand Environment and Conservation Council
BLM	Biotic Ligand Model
CCC	Criterion Continuous Concentration (US EPA chronic criterion)
CMC	Criterion Maximum Concentration (US EPA acute criterion)
CSIG	Coastal Special Interest Group (Special Interest Group of Regional Council staff)
Cu	Copper
DOC	Dissolved organic carbon
DOM	Dissolved organic matter
DGVs	Default guideline values
NOF	National Objectives Framework
NOM	Natural Organic Matter
NPS	National Policy Statement
NPS-FM	National Policy Statement for Freshwater Management
PAUP	Proposed Auckland Unitary Plan
SWIM	Surface Water Integrated Management (Special Interest Group of Regional Council staff)
SoE	State of the Environment
TMFs	Toxicity modifying factors
TV	Trigger value
US EPA	United States Environmental Protection Agency
WER	Water effect ratio
Zn	Zinc

Glossary

Term	Definition (reference source)
Attribute	Is a measurable characteristic of fresh water, including physical, chemical and biological properties, which supports particular values (MfE 2014a)
Attribute state	Is the level to which an attribute is to be managed for those attributes specified in Appendix 2 of MfE (2014a)
Compulsory values	Mean the national values relating to ecosystem health and to human health for recreation for which a non-exhaustive list of attributes is provided in Appendix 2 of (MfE 2014a)
Contaminant	Biological (e.g., bacterial and viral pathogens) or chemical (e.g., toxicants) introductions capable of producing an adverse effect in a water body. (ANZECC 2000).
Ecological health	Indicates the preferred state of sites that have been modified by human activity, ensuring that their ongoing use does not degrade them for future use. (Karr 1999)
Guideline (water quality)	Numerical concentration limit or narrative statement recommended to support and maintain a designated water use. (ANZECC 2000)
Hardness	The concentration of all metallic cations, except those of the alkali metals, present in water. In general, hardness is a measure of the concentration of calcium and magnesium ions in water and is frequently expressed as mg/L calcium carbonate equivalent. (ANZECC 2000)
Limit	A limit is the maximum amount of resource use available, which allows a freshwater objective to be met. (MfE 2014a)
(Management) Objective	Describes the intended environmental outcomes(s) (definition from National Policy Statement for Freshwater Management). Freshwater objectives are set in regional planning documents and describe the desired state of the water body, having taken into account all desired values.
Standard (water quality)	An objective that is recognised in enforceable environmental control laws of a level of government.

Term	Definition (reference source)
State	A range in the level of an attribute that may be described as a narrative or numerically. Four different states are specified for attributes (A, B, C or D). The term ‘band’, instead of the term ‘state’, was previously used in the development of the National Objectives Framework.
Toxicant	A chemical capable of producing an adverse response (effect) in a biological system, seriously injuring structure or function or producing death. Examples include pesticides, heavy metals and biotoxins. (ANZECC 2000)
Toxicity	The inherent potential or capacity of a material to cause adverse effects in a living organism.
Trigger value (TV)	These are the concentrations (or loads) of the key performance indicators measured for the ecosystem, below which there exists a low risk that adverse biological (ecological) effects will occur. They indicate a risk of impact if exceeded and should ‘trigger’ some action, either further ecosystem specific investigations or implementation of management/remedial actions. (ANZECC 2000)
Uses	The uses to/for a water body – equivalent to Values.
Value	a) any national value; and b) includes any value in relation to freshwater, that is not in Appendix 1, which a regional council identifies as appropriate for regional or local circumstances (including any use value). (MfE 2014a)
Water quality criteria	Scientific data evaluated to derive the recommended quality of water for various uses. (ANZECC 2000)
Water quality objective	A numerical concentration limit or narrative statement that has been established to support and protect the designated uses of water at a specified site. It is based on scientific criteria or water quality guidelines but may be modified by other inputs such as social or political constraints. (ANZECC 2000)

1 Introduction

1.1 Background

'Urban stream syndrome' and degraded ecological health are significant issues in Auckland streams (Bishop et al. 2015). Exceedances of ANZECC (2000) water quality guidelines for copper and zinc within streams indicate copper and zinc may be key contributors to poor ecological health in the urban area (Mills & Williamson 2008). Copper (Cu) and zinc (Zn) levels in stream and coastal sediments have also been identified as significant environmental issues in Auckland, primarily in urban areas (Bishop et al. 2015; Mills & Williamson 2008). Projected urban development has the potential to deliver further adverse effects if Cu and Zn limits are not set. Stormwater management is a key issue identified in the Auckland Unitary Plan, with provisions included to reduce contaminants including Cu and Zn. Cu and Zn management in Wellington and Christchurch may also be required to reduce the elevated concentrations in streams in these centres (Margetts & Marshall 2015; Perrie et al. 2012).

The National Policy Statement for Freshwater Management 2014 (amended 2017) (hereafter referred to as NPS-FM) includes key water quality attributes in the National Objectives Framework (NOF), but attributes relating specifically to urban water quality issues are not currently included. Auckland Council identified a need to progress Auckland-specific urban water quality attributes, rather than wait for guidance from Ministry for the Environment (MfE), an approach endorsed by MfE.

The NPS-FM (MfE 2017) specifically allows councils to identify attributes in addition to those in the National Objectives Framework (NOF) (MfE 2017). These attributes can be applicable to NOF values or any other freshwater values. Along with sediment, temperature and macrophytes, Cu and Zn have been assessed as two of the top five regional attributes for development by Auckland Council.

The overall goal is to develop Auckland-specific regional attributes for Cu and Zn in alignment with the NOF, which could then be adopted or adapted to other parts of New Zealand, particularly the urban centres of Wellington and Christchurch. This report delivers the first step in this process by summarising existing information and providing an example of how an attribute tables could be developed for Zn and Cu. The report also identifies additional work required for completion of attribute tables.

This report proposes Cu and Zn "strawman" (or example) attribute tables, that until superseded, can provide initial strategic direction for a number of Auckland Council freshwater management outcomes related to Cu and Zn management (e.g., via the Auckland Council's Freshwater Management Tool currently under development). This report will assist with achieving the objectives of a number of Auckland Council and national level strategic directions, research priorities and policies, including the Auckland Plan, Auckland Unitary Plan, biodiversity strategy, New Zealand Coastal Policy Statement and the Auckland Council, SWIM and CSIG research strategies, either directly through recommendations on freshwater management or indirectly through freshwater outcomes affecting the coastal receiving environment.

As noted in the preface, the bulk of this work was undertaken in 2015 and the findings provided to Auckland Council in a working paper (Williamson et al. 2015), with further analyses undertaken in 2016/2017. This discussion paper incorporates both these phases of work and outlines remaining gaps in knowledge and tasks that should be undertaken in any further development of Cu and Zn attributes, by Auckland Council or other organisations such as MfE.

Auckland Council's Research and Evaluation Unit discussion papers are intended to generate and contribute to discussion on topical issues related to Auckland. They represent the views of the authors and not necessarily those of Auckland Council.

1.2 Scope

The scope of this project included:

- Expert recommendations on how best to integrate Cu and Zn into the format of an ecosystem health attribute table for the Auckland region in alignment with the NOF framework (i.e., for incorporation into NPS-FM implementation).
- Understanding what is required to provide scientific robustness and technical defensibility to attribute tables for Cu and Zn including bioavailability aspects and identification of significant implementation and management considerations.
- Outlining what is required for completion of attribute tables in subsequent work.

The following items are out of scope:

- Detailed consideration of costs involved in implementing the attribute.
- Human or domestic / livestock animal health aspects e.g. metals in surface or groundwater for contact recreation, human consumption, stock watering or aquaculture.
- Any additional monitoring or sampling required to further refine concentrations.
- A final attribute table with specific numeric and narrative attribute states.

In developing attributes it is necessary to remain cognisant of aspects such as implementation (also considering the PAUP), limit setting, connection with the coastal receiving environment, monitoring and cost.

1.3 Attribute requirements

NOF attributes in the NPS-FM are associated with various *aspects* of freshwater environments that need to be managed to support and sustain values such as ecosystem health. The existing NPS-FM attributes are associated with aspects that represent nationally important freshwater management issues, including trophic state, toxicity status and human pathogens. Attributes support the definition of numeric freshwater objectives and the development of associated limits and actions (Figure 1-1).

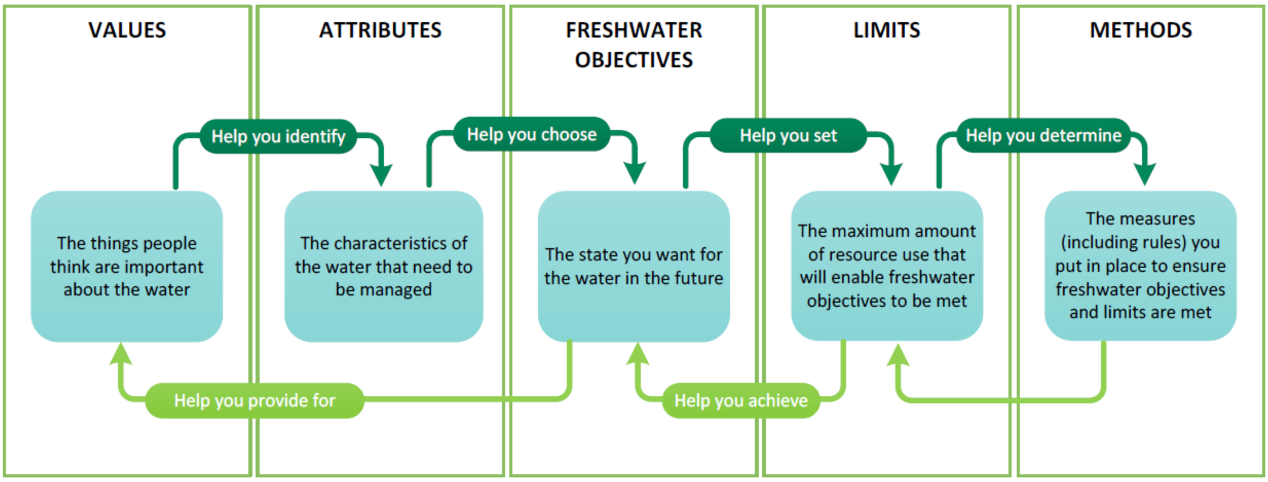


Figure 1-1 Generalised diagram of the links between values, objectives, limits and management actions (from MfE 2018).

The matters that were considered before including an attribute in Appendix 2 of the Freshwater NPS 2014 included (MfE 2014b):

1. Link to the national value
    - Is the attribute required to support the value?
    - Does the attribute represent the value?
2. Measurement and band thresholds
    - Are there established protocols for measurement of the attribute?
    - Do experts agree on the summary statistic and associated time period?
    - Do experts agree on thresholds for the numerical bands and associated band descriptors?
3. Relationship to limits and management
    - Do we know what to do to manage this attribute?
    - Do we understand the drivers associated with the attribute?
    - Do quantitative relationships link the attribute state to resource use limits and/or management interventions?
4. Evaluation of current state of the attribute on a national scale
    - What do we know about the current state of the attribute at a national scale?
    - Is there data of sufficient quality, quantity and representativeness to assess the current state of the attribute on a national scale?

5. Implications of including the attribute in the NOF
    - Do we understand/can we estimate the extent (spatial), magnitude, and location of failures to meet the proposed bottom line for the attribute on a national scale?
    - Do we understand the implications for socio-economic impacts?

These matters are also applicable in relation to developing attributes for regional use, albeit with modifications relating to the evaluation of current state on a regional scale rather than a national scale.

1.4 Outline of this discussion paper

This discussion paper describes the progress towards the attribute tables in the following chapters.

Chapter 2: Summary of ANZECC and USEPA guidelines that could be used to provide numerical objectives in the attribute table, their current revision and discussion of bioavailability and how this can be incorporated into guidelines and attribute tables.

Chapter 3: An analysis of the choice of sample statistics employed in attribute tables (which compare monitoring data to numerical objectives), a “strawman” attribute table proposed by Auckland Council and the testing of Auckland stream data against this table.

Chapter 4: A detailed analysis of the state of Auckland freshwater stream data from state of the environment monitoring sites and from a study in the Twin Streams (Waitākere) catchment. This includes analysis of land use effects, land use thresholds, dissolved/total relationships, seasonal effects and trends. Comprehensive plots and tables of statistics from this analysis form the basis for testing attribute tables.

Chapter 5: Preliminary analysis of how Cu and Zn concentrations vary with flow and why this is important to understand.

Chapter 6: Summary of this report and recommendations for next steps towards attribute development.

2 Thresholds for Copper and Zinc

2.1 Introduction

Attribute tables require numerical thresholds to set attribute bands: A, B, C and D (below the national bottom line). Attributes for toxic contaminants should protect aquatic organisms from both chronic (long-term) and acute (short-term) exposures. The attributes developed for other toxic contaminants (nitrate and ammonia) are partly based on guidelines that were already in existence, using the ANZECC (2000) guidelines to protect from chronic toxicity. Threshold effect concentrations were developed specifically for the NOF to protect from short-term exposures. For Cu and Zn, chronic guidelines are also available in ANZECC (2000) and these are reviewed in this section along with a brief discussion of the update of these guidelines. This section also includes a review of US EPA criteria for Cu and Zn. Within this section, the effects of toxicity modifying factors are also described, and methods to incorporate these into water quality guidelines are discussed. The current guidelines for Cu and Zn have also been summarised in recent reports for freshwater (Hickey et al. 2015) and coastal waters (Williamson et al. 2015).

2.2 The ANZECC (2000) guidelines

The ANZECC (2000) guidelines provide comprehensive guidance for toxicity assessment of Cu and Zn on aquatic fauna. As with all the ANZECC guidelines, they list trigger values and provide a decision tree approach for assessing toxicity or they propose users develop site-specific guideline values.

The first step in any assessment is choosing a suitable level of protection, which depends on the ecosystem condition. ANZECC (2000) recognised three types of ecosystem conditions:

1. high conservation/ecological value
2. slightly to moderately disturbed ecosystems
3. highly disturbed ecosystems.

Appropriate levels of protection must be selected, often in consultation with stakeholders, and for the above three ecosystem conditions are typically: 1) 99%, 2) 95%, 3) either 90% or 80% (see ANZECC (2000)). Table 2-1 summarises the ANZECC guideline trigger values for Cu and Zn in freshwaters for various levels of protection. These trigger values provide protection from chronic (long-term) toxicity based on toxicity studies conducted over a period representing chronic exposure (typically > 96 hours in the 2000 version guidelines).

Table 2-1 The ANZECC (2000) guidelines for Cu and Zn.

	ANZECC Level of protection (chronic)			
	99%	95%	90%	80%
Cu	1 µg/L	1.4 µg/L	1.8 µg/L	2.5 µg/L
Zn	2.4 µg/L	8 µg/L	15 µg/L	31 µg/L

Values for all guidelines at hardness of 30 mg $CaCO_3$/L (standard hardness in ANZECC (2000)).

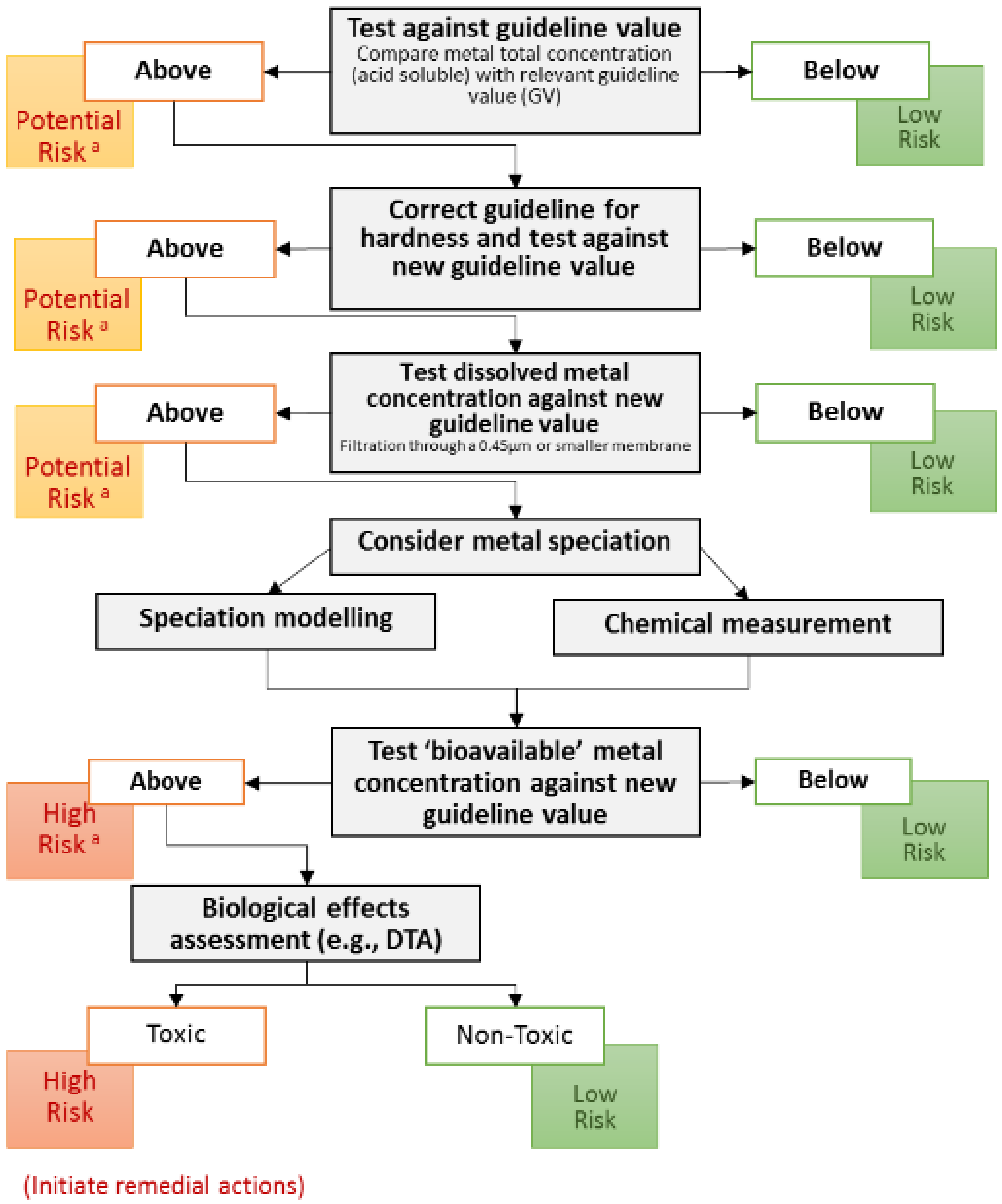
The ANZECC (2000)[1] guidelines specify that for toxicants, the 95th percentile of the monitoring data should be below the guideline value. However, in practice, the guidelines are frequently used for stable flow conditions and many users choose to compare an “average” summary statistic such as the median.

The trigger values are usually compared with concentrations of Zn and/or Cu measured in surface waters but they can be compared to modelled concentrations.

The ANZECC (2000) guidelines are termed ‘trigger values’ (TVs) below which there is a low risk that adverse biological effects will occur to the degree of community protection required (e.g., 80->99%). They are designed to be used in conjunction with professional judgement, to provide an initial assessment of the state of the water body and to trigger multiple possible responses, according to the decision tree (Figure 2-1). These range from simple additional analyses to more complex speciation measurement or modelling, or direct toxicity assessment. However, the costs of such further investigations are likely to be much less than trying to reduce Cu and Zn concentrations in streams.

Because of the decision tree approach provided by ANZECC (2000), the trigger values serve largely for screening exercises, rather than refined estimates of the actual risk of toxicity presented in a waterway. This approach is not likely to be suitable for incorporation into a NOF attribute, where a numeric attribute is required for the attribute table. Therefore, alternative ways to incorporate bioavailability need to be explored (see section 2.5).

[1] See section 7.4.4.2.



[a] *Further investigations are not mandatory; users may opt to proceed to management/remedial action.*

Figure 2-1 Decision tree for metal toxicity guidelines from ANZECC (2000).

2.3 Revision of the ANZECC guidelines

The ANZECC guidelines have been under revision for a number of years and a new website and guidance has been released under the designation of Australian and New Zealand (ANZ) guidelines[2]. The revision includes updating the freshwater Cu and Zn trigger values (now called guideline values), with Ministry for the Environment (MfE) sponsoring the initial work on this. Draft guidelines for these were published in 2016 (Gadd & Hickey 2016a; 2016b) and finalised versions are expected to be available in 2019.

There are a number of differences between the ANZECC (2000) and the updated ANZ guidelines.

- The ANZECC guidelines were published in 2000, and data used was current only up to about 1998. The 2000 Guidelines for Cu and Zn were based on 20 different species. Since then, a number of new studies have been published, including New Zealand studies (e.g., see Figure 2-2 summarising Cu data for native species) and more sensitive species and life stages.
- Both sets of guidelines are based on chronic (long-term) toxicity and so the data collated were restricted to toxicity studies conducted over a period representing chronic exposure. In the ANZECC (2000) guidelines this was typically > 96 hours. In the revised ANZ guidelines this is dependent on each test organism, its life expectancy and the type of toxicity test (e.g., growth or survival). This provides time frames such as ≥ 24 hours for growth tests on algae; and ≥ 21 days for lethal tests on fish (Warne et al. 2018).
- The ANZECC (2000) guidelines were based on No Observed Effect Concentration (NOEC) data (the highest statistically-derived test concentration that does not cause a significant effect in a toxicity test), and on data converted from EC50 concentrations (Effect Concentration 50, where 50 refers to the percentage of organisms affected). The new ANZ guidelines use low effect concentration data (i.e., EC10 data) in preference to NOEC data and avoid the use of converted EC50s where possible (Warne et al. 2018).
- ANZECC (2000) Cu and Zn trigger values were hardness adjusted, and the ANZECC (2000) metal trigger values (TVs) in the original document were given for a hardness of 30 g $CaCO_3/m^3$. Since then conflicting data has been demonstrated for the effect of hardness on Cu toxicity to various species including sensitive water fleas and algae (e.g., Markich et al. 2005; 2006). Concern that hardness corrections would not protect sensitive freshwater species led to the recommendation that revised ANZ Cu guidelines are not hardness-corrected (Batley et al. 2018).
- Instead, dissolved organic carbon (DOC) is now recognised as being very important in modifying Cu toxicity. The draft revised ANZ guidelines for freshwater Cu are therefore DOC adjusted, with a default guideline at a DOC concentration of 0.5 mg/L.

[2] http://www.waterquality.gov.au/anz-guidelines

- For Zn, hardness remains important, and there is increased understanding that pH and DOC are also important toxicity modifying factors (TMFs) and the revised ANZ guidelines are expected to take all three TMFs into account in determining guideline values.

Until the new ANZ guidelines are released, it is difficult to predict the overall effect of these various changes in the derivation process on the final guideline values. It is possible that the default guideline values (DGVs) will be lower than the ANZECC (2000) default trigger values; however, when TMFs are incorporated, the ANZ guideline values may be less conservative at some locations.

As a result of the way toxicity modifying factors are incorporated into the new guidelines, although default guideline values are provided, these are unlikely to be appropriate for most sites, as they represent conditions with very low hardness and DOC. In most cases, an adjusted guideline will be more appropriate. The ANZ guidelines will provide either equations to adjust the guidelines based on TMFs, or look-up tables with differing guideline values. The way these equations and look-up tables are incorporated into an attribute table will need to be considered, although there is an example in the way ammonia guidelines are used in the NOF attribute table, with a look-up table of adjustment factors based on pH.

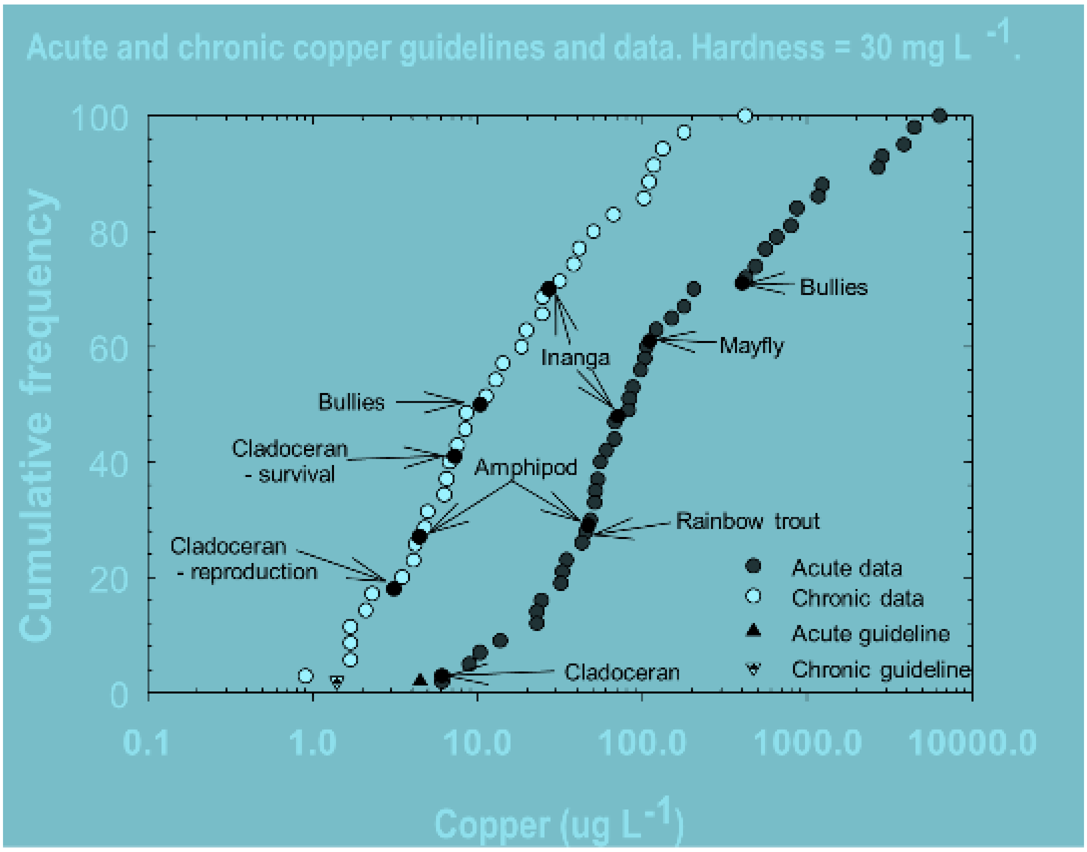


Figure 2-2 Probability plots of acute and chronic copper concentrations (Hickey 2000).

2.4 US EPA criteria

Attribute tables should protect from acute toxicity due to short-term pulses of toxicants, such as might occur from urban stormwater. Acute guidelines are not available in the ANZECC (2000) guidelines, so in New Zealand the US EPA Ambient Water Criteria – Criteria Maximum Concentration (CMC) are often used (US EPA 2007).

The CMC is an estimate of the highest concentration of a material in surface water to which an aquatic community can be exposed briefly without an unacceptable effect (= acute concentration). Note that the Criterion Continuous Concentration (CCC) is an estimate of the highest concentration of a material in surface water to which an aquatic community can be exposed indefinitely without an unacceptable effect (= chronic concentration). The CMC and CCC are just two of the six parts of an aquatic life criterion in the USA; the other four parts are the acute averaging period, chronic averaging period, acute frequency of allowed exceedance, and chronic frequency of allowed exceedance.

Table 2-2. The USEPA acute criteria for copper (Cu) and zinc (Zn)

	USEPA CMC (Acute)	Water chemistry	Reference
Cu	4.3 µg/L	At pH 8, hardness of 30 mg/L, DOC 0.5 mg/L	US EPA (2007)
Zn	42 µg/L	At hardness of 30 mg/L	US EPA (1995)

Although US EPA criteria have been used in New Zealand, it is important to note that in the derivation of the US guidelines they specifically exclude toxicity data for species which are not resident in North America. Species which are invasive in North America are however included, based on this definition. This means that data for New Zealand native species would not be included, unless they are also resident in North America, which few are. Furthermore, the Zn guideline is over 20 years old and there is substantial new toxicity data available. For these reasons, it would be preferable to develop guidelines more specific to New Zealand.

2.5 Incorporating bioavailability into attribute tables

As discussed above, water quality guidelines incorporate bioavailability to a varying degree. The ANZECC (2000) guidelines and the revised ANZ guidelines only include adjustment of guideline values for the major toxicity modifiers. There are other factors that affect speciation and bioavailability that are not considered in those guidelines, as they provide the option for further modelling or measurement of metal speciation. This approach cannot be incorporated easily into a NOF attribute table and as such failure to consider these factors may result in attribute thresholds that are either under-protective to aquatic life or too conservative, requiring substantial management and investment to meet such thresholds. Methods that more fully incorporate bioavailability may be more appropriate for incorporation into a NOF attribute table and such methods are described in this section.

Biotic Ligand Models (BLMs) (Santore et al. 2001; Paquin et al. 2002), such as those used for the US EPA copper criteria, have been developed to predict metal toxicity for aquatic organisms. A BLM incorporates two steps: a) speciation modelling and b) binding to the biotic ligand. The basis for this second part is the toxic mechanism in aquatic animals: Cu toxicity in freshwater fish occurs due to disruptions of ion regulation after binding to gill membranes (the biotic ligand) and similar mechanisms have been demonstrated for other aquatic organisms and other metals.

A BLM forms the basis of US EPA's 2007 national recommended 304(a) freshwater criterion for copper (US EPA 2007), both in terms of developing the criteria and for using it [3]. When using the criteria, users can either use the default, or use the model to derive a site-specific WQC based on water quality measurements from their field site such as pH, DOC, major ion concentrations (e.g., calcium, magnesium, chlorine) and alkalinity or Dissolved Inorganic Carbon (DIC). The BLM allows regulators and dischargers to account for the effect of water chemistry on the toxicity of metals to aquatic organisms. In particular, the BLM-based guideline is strongly affected by DOC (see Table 2-3).

Table 2-3 Biotic ligand model (BLM) based Cu Criterion Maximum Concentration (CMC) values for varying concentrations of dissolved organic carbon (DOC) at pH 7.0 and hardness of 80 mg/L $CaCO_3$ (Smith et al. 2015).

DOC (mg/L)	BLM-based CMC (µg/L)
2	4.4
4	8.8
8	18.0
16	37.0

(Note the CMC for 30 mg/L $CaCO_3$ is 4.3 µg/L Cu (Tables 2.1, 4.1)).

The currently available software tools for undertaking Biotic Ligand Model calculations (e.g., the one developed by HydroQual, now Windward Environmental[4]) can be data-demanding (more than 10 physico-chemical input parameters are required to run the models), time-consuming and insufficiently user friendly. These drawbacks are significant barriers to the widespread regulatory acceptance and implementation of Biotic Ligand Models for routine use. In those jurisdictions where the full BLMs are considered difficult to incorporate into regulation, 'user-friendly' tools have been developed, including:

[3] https://www.epa.gov/wqc/aquatic-life-criteria-copper

[4] http://www.windwardenv.com/biotic-ligand-model/#

- bio-met: a bioavailability tool developed in Europe and England in conjunction with the metal associations;
- PNEC-pro, developed in Europe;
- Cu-PNEC estimator, developed in Europe in association with the European Copper Institute; and
- M-BAT: a Metal Bioavailability Assessment Tool developed in the UK.

In New Zealand there are additional barriers to the use of a BLM, or one of its simplifications including a) lack of validation of the models with native species; and b) confirmation that the range of water chemistries (e.g., range in hardness) for which the models were developed is appropriate to New Zealand waters. However as previously mentioned there are also implications for not incorporating bioavailability adequately into a NOF attribute.

Whether the bioavailability is incorporated through lookup tables based on key TMFs, or on BLMs, additional water chemistry will need to be measured in urban streams. Auckland Council began measuring DOC, hardness and pH in their state of the environment (SoE) programme in July 2018. Greater Wellington Regional Council and Christchurch City Council also now measure these in their SoE programmes. In some cases, surrogates for the TMFs may be appropriate and cheaper to monitor, for example conductivity may be a useful surrogate for hardness; UV absorbance and iron can be useful surrogates for DOC. However, data will first need to be collected on each of these to verify the relationships and this may need to be undertaken for each stream.

2.6 Recommendations

When the revised ANZECC guidelines for Cu and Zn are available, these should be used as thresholds in the attribute tables in preference to the ANZECC (2000) trigger values. This is in light of the expanded toxicity database, new ANZECC guidance for chronic definitions, endpoints, statistical fitting, and toxicity modifying factors. If acute guidelines are developed, these could also be used for thresholds in preference to US EPA CMC values.

The revised ANZECC guidelines are likely to incorporate pH, hardness and DOC, rather than just hardness as in ANZECC (2000). These factors will need to be measured in urban streams to provide information on their concentration for use in adjusting guidelines to be site-specific, or to model bioavailable metals.

At this stage there is insufficient information for Auckland to determine how these factors vary spatially and temporally and under differing flow conditions. Christchurch City Council already holds data on these factors and these could be examined to determine variation in water chemistry over storms and implications to Cu and Zn speciation, bioavailability and criteria. (Note that the Christchurch data does not have flow measurement, so this analysis would need to be done identifying high flows by TSS and conductivity, which may be a limitation). Alternatively, when AC has acquired sufficient data on these TMFs, this should be analysed.

This information will assist in determining whether TMFs need to be determined in every stream and at each time of sampling; whether surrogates could be used (such as conductivity for hardness); and whether there are characteristic values that can be used for Auckland's urban streams.

World-wide, metal toxicity guidelines are becoming increasingly complex, dependent on multiple toxicity modifying factors, and incorporating models to assess bioavailability. Investigations as to whether the chemical is posing a real risk or not usually follow application of relevant decision trees. This approach is relatively complex, and not suitable to simple pass/fail concentration values. The way to incorporate bioavailability into attribute tables needs to be carefully considered to ensure that attribute thresholds are not unnecessarily restrictive (e.g., if comparing dissolved metals rather than bioavailable) but also are not extremely complex to understand or implement. There are several additional options for incorporating bioavailability modelling into attribute development including:

- Revising the ANZECC guidelines further by using the full BLM in the development of thresholds used in the attribute tables (i.e., using a BLM to normalize toxicity data before generating an SSD and guideline value);
- Using a BLM or simplified BLM tool to estimate bioavailable concentrations to compare to a non-adjusted value in the attribute table;
- Develop a tool like biomet that provides band thresholds for local water chemistry conditions.

A first step towards determining whether the above is necessary would be to use the data from Christchurch City Council and the Bio-Met or BLM model to predict water quality criteria. This will help to establish the sensitivity of the criteria, for the range in water chemistry observed in NZ. This range could also be compared to the range in guideline values from the revised ANZECC guidelines based on the same values of DOC, pH and hardness.

3 The Attribute Table

3.1 The sample statistics

For an attribute table, sample statistics must be considered: what statistic of the monitoring data set is compared to attribute thresholds. The National Objectives Framework (NOF) attribute tables developed to date use a variety of statistics, such as a seven-day mean minimum for dissolved oxygen, a median for several attributes, and 80^{th} percentile for cyanobacteria. Several attributes employ two statistics, including attributes for nitrate and ammonia, associated with toxicity and most relevant to Cu and Zn. One of these statistics represents the “average” condition and one the “maximum” condition.

3.1.1 The “average” condition

Most of the attribute tables use a median sample statistic to represent the “average” condition. This statistic represents the value below which 50% of observations may be found and is not skewed by high (or low) concentrations like a mean statistic. The medians are aimed at assessing long exposure times and under settled freshwater conditions (baseflow conditions).

3.1.2 The “maximum” condition

The maximum condition in attribute tables can serve two purposes. One is to provide a maximum allowable concentration for each attribute band (to ensure the range of in-stream concentrations is not excessively broad). The second purpose is to assess acute conditions. An acute guideline is frequently used for the bottom-line threshold. In the National Objectives Framework (NOF) developed to date the maximum condition varies between contaminants. The ammonia attribute table uses the maximum whereas the nitrate attribute table uses the 95^{th} percentile.

As above, the “maximum condition” could mean using maxima, or it could mean using other statistics, such as the 95^{th} percentile or 90^{th} percentile. These statistics exclude rarely-occurring, unusually high concentrations and ‘desensitize’ the assessment to the possible bias of short-lived, very high concentrations that may not be having a significant effect (i.e., due to a very low frequency or a very short time of exposure, or which may be due to sample/analysis errors).

Some form of maximum condition is likely to be needed for Cu and Zn in urban streams to protect from acute effects. In urban catchments, storm events wash metals deposited on roads or roofs into receiving waters and concentrations can rise with the “first flush” and then fall as the bulk of the deposited metals are washed away (e.g., Shamseldin 2011). The relationship between in-stream contaminant concentrations and rainfall/stream flow can be complex and may vary considerably at different locations within, and between, catchments, depending on pre-storm conditions, mobilisation of contaminants, the rate of increase in flow, the flow rate, flushing and dilution. The highest concentrations can be associated with the rising stage in small catchments. A maximum condition may be used to protect against these conditions.

3.2 Thresholds

ANZECC guidelines lend themselves to developing attribute tables because ANZECC guidelines are based on chronic effects and describe multiple levels of protection (99%, 95%, 90%, 80%) which can be used for the different attribute grades. Attribute grades A, B, C could be based on chronic effects. Acute effects are generally regarded as below the bottom line and thus the US EPA CMC could be used as a threshold here.

Using the ANZECC levels of protection, each band could be defined as in Table 3-1. Thus the bands use a mixture of protection levels and utilise four levels of protection, however, there are mixed levels of protection in each band. Such levels of community protection accord well with the guidance on nitrate and ammonia toxicity (e.g., near-equivalent levels of community protection within bands A-C therein

Table 3-1 The protection levels (PL) in each band of the strawman attribute tables.

Grade	Median	Maximum	Implication
A	<99% PL	<95% PL	50% time protect ≥99% species from chronic toxicity 100% time protect >95% species from chronic toxicity
B	<95% PL	<90% PL	50% time protect 99-95% species from chronic toxicity 100% time protect >90% species from chronic toxicity
C	<90% PL	<80% PL	50% time protect ≥90% species from chronic toxicity 100% time protect 80% species from chronic toxicity
D	>80% PL	>EPA CMC	50% time protect 80% species from chronic toxicity Acute toxicity may occur

Another and simpler approach would be to make use of a maximum value for the range. For example, Table 3-2. However, any decisions on these tables should be made after completion of the further recommended work in section 6.

Table 3-2 Alternative numerical and narrative objectives.

Grade	Maximum	Implication
A	<99% PL	100% of time >99% species from chronic toxicity
B	> 99% and <95% PL	100% time protect >95% species from chronic toxicity
C	>95% and <80% PL	100% time protect 80% species from chronic toxicity
D	>EPA CMC	Acute toxicity potentially occurs

3.3 Straw man attribute tables

A “straw man” attribute table was developed for dissolved Cu (Table 3-3) and for Zn (Table 3-4). Concentrations are specified as dissolved as these more closely represent the bioavailable portion and are consistent with ANZECC (2000) and US EPA guidelines. This table is not the final version to be used by Auckland Council, but rather a working table used to evaluate attribute options. The values in this straw man table that are based on the ANZECC (2000) guidelines should be replaced by the revised Cu and Zn ANZ guidelines when these become available. The revised values may be calculated at different concentrations of TMFs and values most appropriate to Auckland urban streams could be used in the tables. Similarly, if acute guidelines are derived following the ANZ procedure, then these should replace the values in this table based on the USEPA CMC.

This straw man attribute table could be amended for:

- Updated guideline values
- Different levels of protection (99%, 95%, 90%, 80%)
- Different measurement statistics (e.g., means instead of medians; 95^{th} percentiles instead of maxima)
- Allowances for bioavailability, for example modifying values based on other TMFs or calculating bioavailable concentrations based on the Biotic Ligand Model.

Table 3-3 Straw man Cu attribute table

Value	Ecosystem health		
Freshwater Body Type	Lakes and rivers		
Attribute	Dissolved Copper (Toxicity)		
Attribute Unit	µg DCu/L (micrograms of dissolved Copper per litre)		
Attribute State	Numeric Attribute State		Narrative Attribute State
	Annual Median	Annual Maximum	
A	≤1	≤1.4	99% species protection level: No observed effect on any species tested
B	>1 and ≤1.4	>1.4 and ≤1.8	95% species protection level: Starts impacting occasionally on the 5% most sensitive species
C	>1.4 and ≤2.5	>1.8 and ≤4.3	80% species protection level: Starts impacting regularly on the 20% most sensitive species (reduced survival of most sensitive species)
National Bottom Line	2.5	4.3	
D	>2.5	>4.3	Starts approaching acute impact level (ie risk of death) for sensitive species

Values for this metal are here expressed as a function of hardness (mg/L) in the water column, consistent with ANZECC (2000) and the value given here corresponds to a standard hardness of 30 mg $CaCO_3$/L. Criteria values for other hardness may be calculated as per the equation presented in the ANZECC (2000) guidelines. The National Bottom Line for the annual maximum is based on US EPA CMC.

Table 3-4 Straw man Zn attribute table

Value	Ecosystem health		
Freshwater Body Type	Lakes and rivers		
Attribute	Dissolved Zn (Toxicity)		
Attribute Unit	µg DZn/L (micrograms of dissolved Zinc per litre)		
Attribute State	Numeric Attribute State		Narrative Attribute State
	Annual Median	Annual Maximum	
A	≤2.4 (50% pro)	≤8 (95% pro)	99% species protection level: No observed effect on any species tested
B	>2.4 and ≤8	>8 and ≤15	95% species protection level: Starts impacting occasionally on the 5% most sensitive species
C	>8 and ≤31	>15 and ≤42	80% species protection level: Starts impacting regularly on the 20% most sensitive species (reduced survival of most sensitive species)
National Bottom Line	31	42	
D	>31	>42	Starts approaching acute impact level (ie risk of death) for sensitive species

Values for this metal are here expressed as a function of hardness (mg/L) in the water column, consistent with ANZECC (2000) and the value given here corresponds to a standard hardness of 30 mg $CaCO_3$/L. Criteria values for other hardness may be calculated as per the equation presented in the ANZECC (2000) guidelines. National Bottom Line for annual maximum based on US EPA CMC.

3.4 Testing the attribute table

When comparing dissolved metal concentrations for urban stream sites as measured from 2005 to 2014 (Table 4-4) with the straw man tables, Auckland urban streams will overall be classed as ‘C’ or ‘D’ state for Cu depending on the sample statistic finally adopted, and ‘D’ state for Zn, regardless of statistic (Table 3-5). For both metals, the maximum condition provides the lowest attribute state and is one or two states lower than the state based on the median.

The rural streams would be classed as ‘D’ for both Cu and Zn based on maximum concentrations, but would meet A, B or C states if 90-95 percentiles were used instead of maximums. Exotic forest streams would be classed an A state for Cu regardless of the statistic used, but either B or C states for Zn. Native forest streams would be classed A state for both Cu and Zn.

Table 3-5 Comparing overall dissolved Zn and Cu concentrations with strawman attribute tables.

	Annual* Median	Annual* maximum based on:			Overall attribute state†
Metal		**Maximum**	**95th percentile**	**90th percentile**	
Copper					
Urban streams	B	D	C	C	D or C
Rural	A	D	C	B	B or C or D
Exotic forest	A	A	A	A	A
Native forest	A	A	A	A	A
Zinc					
Urban streams	C	D	D	D	D
Rural	A	D	B	A	A or B or D
Exotic forest	A	C	C	B	B or C
Native forest	A	A	A	A	A

Note: * The data used to prepare this table comes from the monitoring period July 2005 to September 2014, not a single annual period. † Overall state based on lowest of annual median and maximum states.

Further analysis of the attribute states for individual streams (Table 3-6) shows that for Cu the overall attribute state would be C for all urban streams. For zinc, the overall state would be D for most streams (based on using the 95th percentile). Lucas Creek and Oakley Creek are the only two streams that would not be below the national bottom line in this example. The tests suggest that most urban streams will fall below the national bottom line for Zn.

Table 3-6 Comparing dissolved Zn and Cu concentrations in individual streams with straw man attribute tables*.

	Copper			Zinc		
Site	Annual* Median	Annual* maximum†	Overall attribute state	Annual* Median	Annual* maximum†	Overall attribute state
Urban						
Avondale Stream	C	C	C	C	D	D
Lucas Creek	B	C	C	B	B	B
Oakley Creek	C	C	C	C	C	C
Omaru Creek	C	C	C	D	D	D
Otaki Creek	B	C	C	C	D	D
Otara Creek (East Tamaki)	B	C	C	C	D	D
Otara Creek (Kennell Hill)	B	C	C	C	D	D
Oteha Stream	B	C	C	C	D	D
Pakuranga Creek (Botany Rd)	B	C	C	C	D	D
Pakuranga Creek (Greenmount Drive)	B	C	C	C	D	D
Puhinui Stream	C	C	C	C	D	D
Rural						
Kumeu River	A	C	C	A	B	B
Mahurangi River (Water Supply)	A	A	A	A	A	A
Makarau River	A	A	A	A	A	A
Matakana River	A	A	A	A	A	A
Okura Creek	A	C	C	A	B	B
Papakura Stream	A	B	B	B	B	B
Papakura Stream (Alfriston Rd)	A	B	B	B	B	B
Vaughan Stream	A	C	C	B	B	B
Wairoa River	A	A	A	A	A	A
Waiwera River	A	A	A	A	A	A
Exotic forest						
Mahurangi River (Forestry HQ)	A	A	A	A	A	A
Riverhead Forest Stream	A	A	A	B	C	C
Native forest						
Nukumea Stream	A	A	A	A	A	A

Note: * The data used to prepare this table comes from the monitoring period July 2005 to September 2014, not a single annual period. † Annual maximum is based on 95th percentile in this example.

3.5 Implications of the straw-man attribute

It appears that the choice of statistic for the "maximum" has the greatest impact on the grading of Auckland streams as comparisons to this condition provide lower attribute gradings than the median statistic/thresholds. If maxima (or 90th or 95th percentiles) were specified in the table, the majority of urban streams will 'fail' based on Zn concentrations and many will also fail based on Cu concentrations. More work needs to be undertaken before the "maximum'' condition can be decided on: both in terms of the statistic used (e.g., maximum or 95th percentile) and in terms of the thresholds used.

- If true maximum samples are specified (e.g., during the rising stage of storms), most urban streams would fail, but such a specification places greater emphasis on more costly and challenging sampling programmes to ensure this maximum is measured accurately.
- Are the maximum concentrations of ecological importance? First flush can result in rapid rise and decline of Zn and Cu over the storm peak, which themselves are short in duration in the highly flashy urban streams. Does exposure of aquatic life to concentrations above EPA CMC (based on four- day toxicity tests) for only a few hours cause toxicity? Or does toxicity occur rapidly under these conditions, even though the toxicity tests run for a longer period?
- Are there maximum conditions of more relevance (e.g., elevated concentrations that occur throughout a storm from rising stage through the storm recession); or are the conditions under which that occurs irrelevant?
- Should the acute criterion be based on time of exposure?
- Should the EPA CMC be used or a different acute threshold?
- If and how should bioavailability be considered and does this also change during storm events?

4 Evaluation of the State of Copper and Zinc in Auckland Streams

4.1 Scope and methodology

4.1.1 Scope

This section describes an exploration of data that was carried out on Auckland streams.

- Compilation of readily available existing data on freshwater Cu and Zn levels in Auckland streams.
- Examination of relationships between metals concentrations and catchment land uses.
- Evaluation of Auckland data against existing guidelines.

The analysis of the Auckland Council SoE monitoring data is presented in sections 4.2 to 4.4. Other data sources are included in Section 4.5.

From this exploration we can understand whether setting attributes for Cu and Zn would affect management of urban streams only (or also rural and forested streams), and whether it would affect management of all urban streams. For these purposes, accurate data on land use was not required and therefore the information most readily available was used (e.g., data from monitoring reports).

4.1.2 Auckland Council river water quality monitoring data

The Auckland Council river water quality SoE monitoring programme provided the principal source of data, up to 2014. The database contained 24 stream monitoring sites with metals data, covering four major land use classes (as given in Lockie and Neale 2014):

- 1 native forest catchment site
- 2 exotic forest sites
- 10 rural sites (mainly pastoral but may include horticultural land use in the catchment)
- 11 urban sites.

The metals data have been collected for up to 19 years for some sites (starting in 1995), but based on quality assurance considerations (mainly ensuring all monitoring data had low and consistent detection limits), we selected data from July 2005 until September 2014 for detailed analysis. Appendix A provides details of the data used.

4.1.3 Twin Streams project data

In addition to the Auckland Council SoE streams' data, we have included supplementary information from the "Twin Streams" project (Diffuse Sources 2004, 2005, 2006). This programme involved monitoring two major streams, the Opanuku and Oratia streams, and one minor stream (Waikumete), in the former Waitākere City area, with monitoring sites located in headwater, rural, peri-urban, and urban locations. The data therefore provide another example of the effects of land use on stream water metals concentrations.

A key difference between the Twin Streams and Auckland Council programmes was that sampling in the Twin Streams project focused on summer "base flow" conditions, deliberating avoiding (as far as possible) storm events.

Another difference is that the Twin Streams programme sampled stream continuums from native bush to fully urban. Also undertaken in the Twin Streams project was an assessment of the relationships between catchment "pressure" indicators (e.g. traffic densities, wastewater overflows, catchment imperviousness) and in-stream water quality (and ecology) effects (Diffuse Sources 2005).

A summary of the Twin Streams findings is presented in section 4.5 and Appendix E.

4.1.4 Land use information

AC categorises each of the stream sites by the dominant land use in the catchment in their reports (e.g., Lockie & Neale 2014). These categories were used for initial exploration in Sections 4.2.1 to 4.2.2.

For the box plots comparing between individual sites, we used the proportion of primary land use by class as obtained from streams trends report; TP336 (Scarsbrook 2007), based on LCDB2 (satellite data from 2001/02). As this has land use for only the sites operating at that time, additional information for the remaining sites was obtained from the 2013 SoE report TR 2014/032 (Lockie & Neale 2014). This reports only a land use classification and some assumptions were made about the proportion of urban land use in the 11 sites for which there was no quantitative data. Only one of these sites was classified as urban (Avondale Stream), the remainder being rural, exotic forest and native forest.

In section 4.2.4, we assessed relationships between metal concentrations and quantitative measures of land use. For this second stage of the analysis, land use information was supplied from the Contaminant Load Model (CLM) and the Land Classification Data Base (LCDB4, representing land cover in 2012/13) by Morphum Environmental. Land use categories used to estimate "urban" land use were anything that would "generate" (or efficiently transport) contaminants as follows:

- CLM: paved surface (commercial, industrial, residential), roofs (commercial, residential, industrial – these are given for four time periods – pre-1995, 1995-2006, after 2006, and unknown), roads (five vehicles per day (vdp) categories).

- LCDB4: built up settlement and transport infrastructure.

The areas in each category for each catchment were summed and divided by the total catchment area to give a per cent urban land use. There were several differences in the per cent land use calculated using each of these methods, and when compared to the data from Scarsbrook (2007).

These differences are presented in Appendix A: Zinc and copper versus land use. For this reason, both the CLM and LCDB4 data are presented separately.

4.1.5 Data processing

Water quality monitoring data was obtained from Auckland Council. There were many data points below detection limits (DLs) particularly for the period from 1995 (where available) to June/July 2005. After this the detection limits decreased from 5 µg/L (ppb) to 0.1 µg/L for soluble Cu and 0.3 µg/L for soluble Zn. Therefore data was generally restricted to the period from July 2005 onwards, with the exception of data used for assessment of trends (section 4.4) and seasonality (section 5.2). There remained a moderate number of samples that were below the detection limits, particularly for the soluble metals (Table 4-1). For the exploratory purposes of this report, data below detection were replaced with values of 0.5 x the detection limit. Several obvious outliers in the data were deleted on the assumption that there were errors in sampling, analysis or transcription.

Table 4-1 Number of values below detection limits (<DL values) in data set from July 2005 to June 2014.

	Cu		Zn	
	Soluble	Total	Soluble	Total
Total no. samples	1735	1734	1735	1734
No. <DL	21	4	63	16
% <DL	1.2	0.2	3.6	0.9

4.1.6 Data analyses

The data was analysed and presented in a series of tables and plots in order to provide an overall assessment of the current state of water quality, and to explore quantitative relationships with drivers including land use. Key summary statistics have also been tabulated for use in assessing data distribution relative to guidelines.

In many of the following sections, the data have been presented as “box and whisker plots” to provide a visual summary of the relationship between metals concentrations at each site, and between land use classes. These show the spread of the data with key statistics shown by the “boxes” (which span the 25 percentile and 75 percentile – i.e. the interquartile range or IQR, with the median concentration shown by a horizontal line within each box) and the “whiskers” (which span the range from the 25 percentile minus 1.5 x IQR and the 75 percentile plus 1.5 x IQR). Values lying beyond the whiskers are considered “outliers” and are shown as “o”s.

Another method used to show data distribution is the "probability plot", which plots the per cent of the samples below given concentrations. These plots readily permit visual assessment of the per cent of samples exceeding guideline concentrations.

Guideline values have been overlain on the box and probability plots to show how the metals concentrations compare with the various ANZECC (2000) guideline species protection levels and with USEPA acute toxicity criteria at each site and/or for each land use class.

Relationships between quantitative estimates of urban land use (using CLM and LCDB4) and soluble Cu and Zn concentrations were assessed using scatterplots with LOWESS smoothers applied. The LOWESS smoothers were set to 0.3 span, modelled in R (R Developers Group, 2018).

4.2 Metal concentrations and the effect of land use

4.2.1 Comparisons of metals concentrations between land use groupings

The effect of land use was explored after grouping sites by catchment land use (using Auckland Council's classification in monitoring reports, e.g., Lockie & Neale 2014) and combining all data for each site from July 2005 to June 2014. The following box plots (Figure 4-1 and Figure 4-2) compare the data distributions between each land use. Note that we have sometimes used expanded scales to show the distributions more clearly around the guideline values. This means these plots are not always showing the samples with highest concentrations (these plots are labelled as "expanded scale").

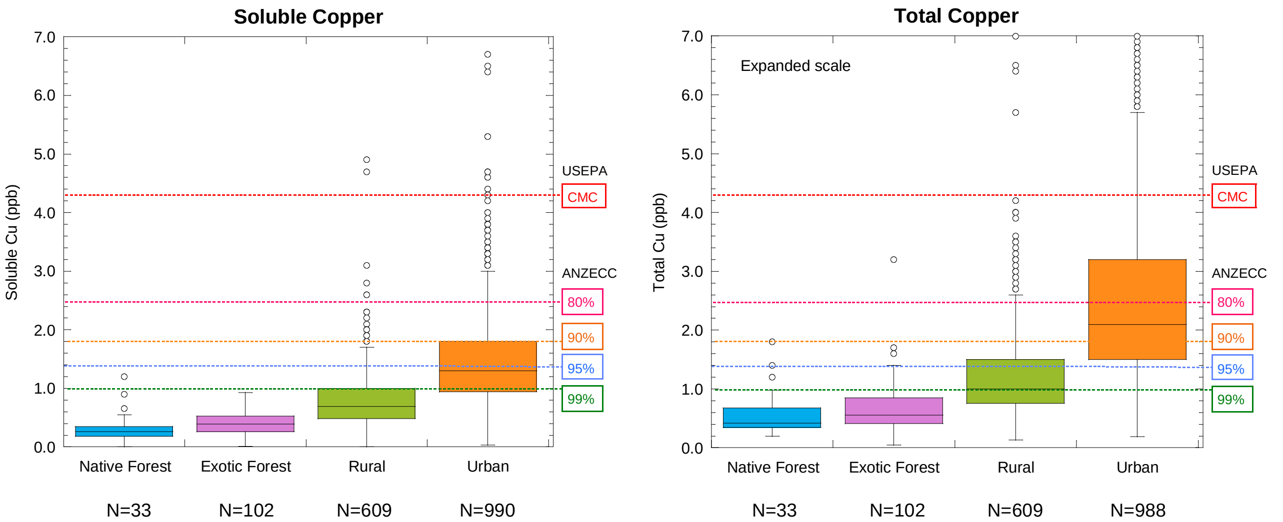


Figure 4-1 Box plots of dissolved and total copper. Samples with total Cu concentrations above 7 µg/L (parts per billion; ppb) are not displayed in the right hand expanded scale plot for total Cu. See Table 4 2 to Table 4 7 for summary statistics, including maxima.

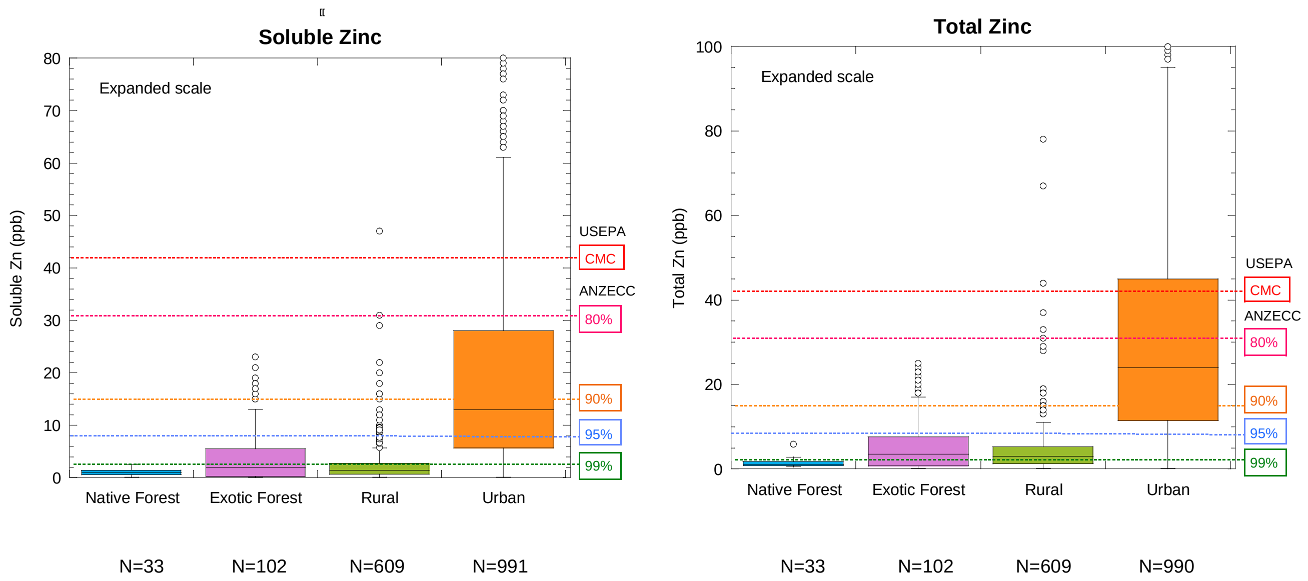


Figure 4-2 Box plots of dissolved and total zinc. Samples with dissolved Zn concentrations greater than 80 µg/L and total Zn concentrations above 100 µg/L (parts per billion, ppb) are not displayed. See Table 4-3 to Table 4-7 for summary statistics, including maxima.

The grouped land use box plots clearly show elevated metal concentrations in urban stream waters. Note however there is much more data for the urban and rural streams, from 11 and 10 sites respectively, compared to only one site for native forest and two sites for exotic forest. This effect is particularly marked for Zn, which is markedly higher in urban catchment streams than in other land uses. Copper showed more gradually increasing concentrations across the native forest-exotic forest-rural-urban land use groups.

Interestingly, the exotic forest group had higher Zn (but not Cu) concentrations than rural streams. This was because of a single site Riverhead Stream, which showed markedly higher concentrations than the other exotic forest site Mahurangi FHQ (see Figure 4-8). The reason for this is unknown and is worth further investigation to assess whether this reflects differences in the natural geology or land practices; or a point source at that site. It would also be worthwhile to examine whether streams in other exotic forests have similar zinc concentrations.

Both metals show frequent exceedance of high levels of protection guidelines (ANZECC 99% and 95%) for urban streams and occasional exceedance in the rural and forested streams. Notably, both soluble and total Cu and Zn concentrations in at least 95% of native forest monitored observations, offered 99% community protection from chronic toxicity, suggesting either the geology of land-cleared areas and/or the practices of those land uses have contributed to elevated metal concentrations in other classes. The data indicate that Zn criteria will probably be the most challenging to meet for urban streams because the soluble Zn concentrations frequently exceed even the low levels of protection guidelines (e.g., the ANZECC 80% species protection level).

The following tables (Table 4-3 to Table 4-7) summarise Cu and Zn concentrations in the Auckland Council stream SoE data (from July 2005 to September 2014) for all sites and grouped by land use (exotic forest, native forest, rural, urban). Data are compared with guidelines (Table 2-1) using the colour coding scheme shown in Table 4-2.

While the contamination of urban streams with Cu and Zn is well understood, the contamination of stream waters in other land uses is far less so. Both Cu and Zn have been used in forest and rural areas in the past and at present (fungicides, animal remedies). There are some other databases available to assess Cu and Zn statistics: for Canterbury streams and rivers, and for Waikato streams and rivers (Waikato Regional Council published reports and unpublished data).

Table 4-2 Colour coding for Tables 4.2 to 4.6 based on guidelines (values are in µg/L or ppb) for Cu and Zn.

Guideline	Copper (soluble and total)	Zinc (soluble and total)
< ANZECC (2000) 99% protection	<1	<2.4
≥ ANZECC (2000) 99% protection	1	2.4
≥ ANZECC (2000) 95% protection	1.4	8
≥ ANZECC (2000) 90% protection	1.8	15
≥ ANZECC (2000) 80% protection	2.5	31
≥ USEPA CMC	4.3	42

Table 4-3 Summary statistics for metal concentrations (µg/L), and guideline exceedance for all land uses.

All Land Uses	Copper		Zinc	
	soluble	total	soluble	total
N of Cases	1734	1732	1735	1734
Minimum	0.01	0.05	0.15	0.15
Median	1.00	1.60	6.2	12.0
Mean	1.21	2.10	16.1	25.7
80% ile	1.70	3.00	23.0	37.0
90% ile	2.30	4.00	38.0	62.0
95% ile	2.80	5.29	58.7	89.8
99% ile	3.92	8.19	141.5	191.6
Maximum	6.70	25.00	370.0	550.0

Table 4-4 Summary statistics for metal concentrations (µg/L), and guideline exceedance for urban streams.

Urban	Copper		Zinc	
	soluble	total	soluble	total
N of Cases	990	988	991	990
Minimum	0.25	0.73	0.49	0.35
Median	1.35	2.20	15.0	26.0
Mean	1.56	2.77	25.9	41.1
80% ile	2.10	3.60	35.0	55.0
90% ile	2.60	4.80	54.4	83.0
95% ile	3.20	5.80	85.9	120.0
99% ile	4.30	11.00	180.0	284.0
Maximum	6.70	25.00	370.0	550.0

Table 4-5 Summary statistics for metal concentrations (μg/L), and guideline exceedance for rural streams.

Rural	Copper		Zinc	
	soluble	total	soluble	total
N of Cases	609	609	609	609
Minimum	0.01	0.13	0.15	0.15
Median	0.67	1.00	1.6	3.3
Mean	0.83	1.33	2.9	5.2
80% ile	1.10	1.80	3.8	6.8
90% ile	1.50	2.40	6.5	11.0
95% ile	1.90	3.10	9.5	16.0
99% ile	2.88	6.44	23.2	39.9
Maximum	6.40	13.00	52.0	78.0

Table 4-6 Summary statistics for metal concentrations (μg/L), and guideline exceedance for exotic forest streams.

Exotic Forest	Copper		Zinc	
	soluble	total	soluble	total
N of Cases	102	102	102	102
Minimum	0.01	0.05	0.15	0.15
Median	0.39	0.56	2.0	3.6
Mean	0.40	0.73	4.2	5.7
80% ile	0.55	0.90	6.6	9.5
90% ile	0.64	1.10	13.6	17.3
95% ile	0.75	1.40	17.4	20.4
99% ile	0.92	5.31	22.0	24.5
Maximum	0.93	7.60	23.0	25.0

Table 4-7 Summary statistics for metal concentrations (μg/L), and guideline exceedance for native forest streams.

Native Forest	Copper		Zinc	
	soluble	total	soluble	total
N of Cases	33	33	33	33
Minimum	0.01	0.20	0.15	0.57
Median	0.26	0.42	1.0	1.1
Mean	0.31	0.56	1.0	1.4
80% ile	0.42	0.70	1.4	2.1
90% ile	0.57	1.02	1.8	2.3
95% ile	0.86	1.37	1.9	2.7
99% ile	1.20	1.80	2.5	5.9
Maximum	1.20	1.80	2.5	5.9

4.2.2 Guideline exceedances by land use groups shown by probability plots

Probability plots show the distribution of the Auckland Council SoE stream data (from July 2005 to September 2014) as the proportion of samples (% of data) that fall below each concentration. When probability plots from data within each land use group are overlain (Figure 4-3 to Figure 4-6), the frequency of exceedance of various guidelines can be visually assessed and land use comparisons made. To make this as useful as possible the plots are sometimes scaled to show the lower guidelines as clearly as possible. In this case they do not necessarily show the full range of the data (hence data – particularly urban land use – may not extend to 100% on the Y-axis; e.g. for Zn in Figure 4-5 and Figure 4-6).

As shown in the previous box plots, the probability plots show the effects of general catchment land use on Cu concentrations, and in particular the effects of urban development on Zn levels.

For soluble Zn (Figure 4-5), approximately 70% of the sample concentrations in urban streams were above the ANZECC 95% protection level, ca. 45% were above the ANZECC 90% level, ca. 25% were above the ANZECC 80% level, and ca. 15% were above the USEPA acute CMC level.

For soluble Cu (Figure 4-3), concentrations generally afforded better community protection than soluble Zn across most land classes – e.g. the ANZECC 80% protection level for soluble Cu in urban streams was only exceeded by ca. 10% of samples, and the 90% level by ca. 30% of the samples.

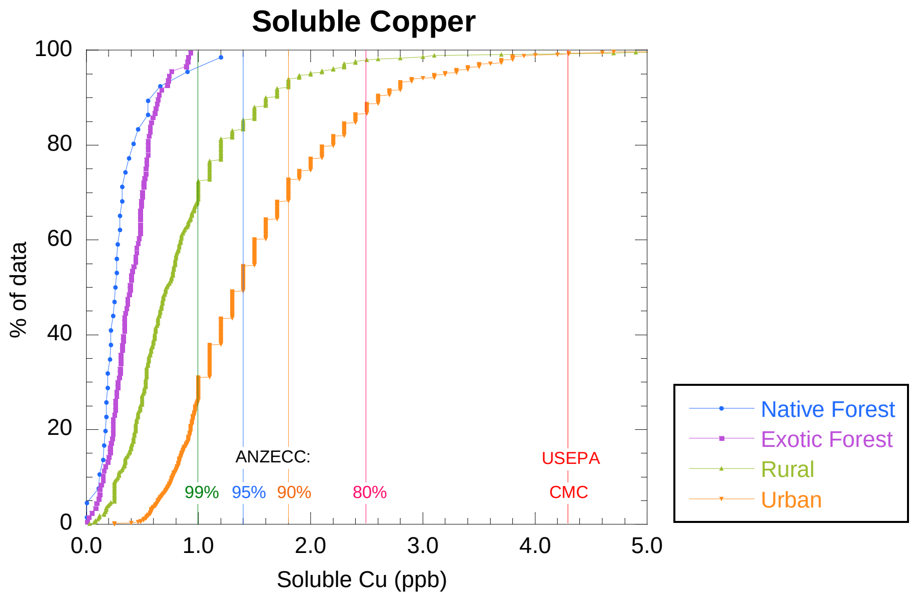


Figure 4-3 Probability plots for soluble copper

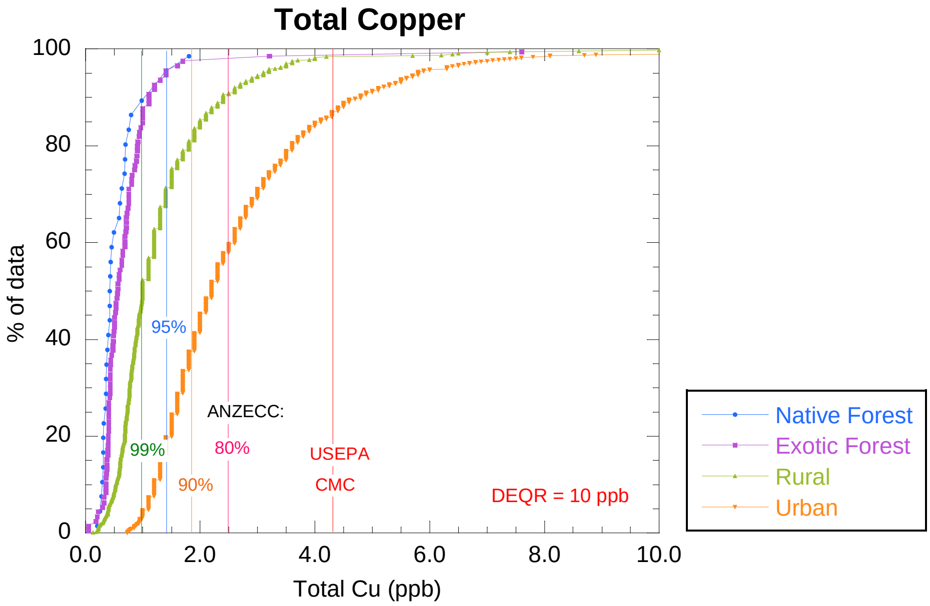


Figure 4-4 Probability plots for total copper

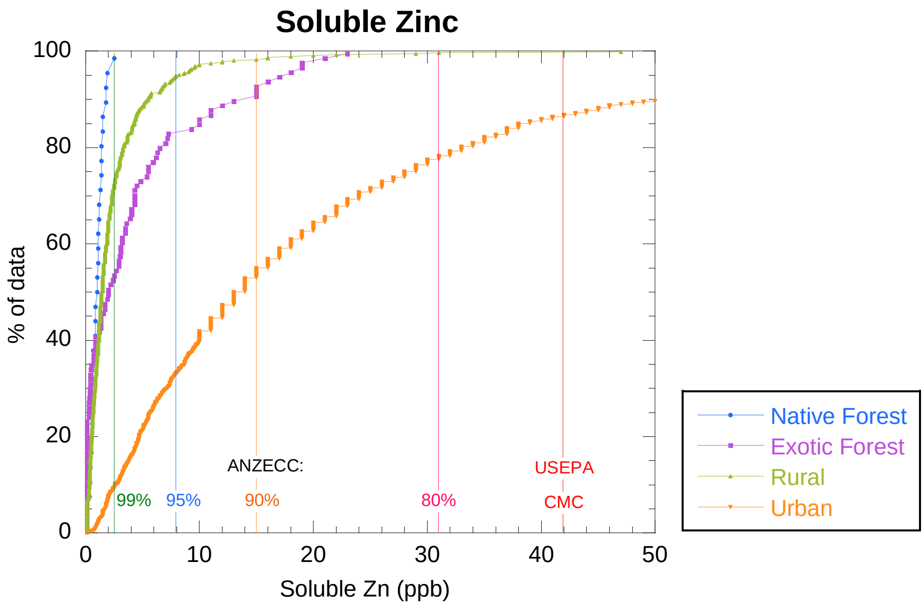


Figure 4-5 Probability plots for soluble zinc

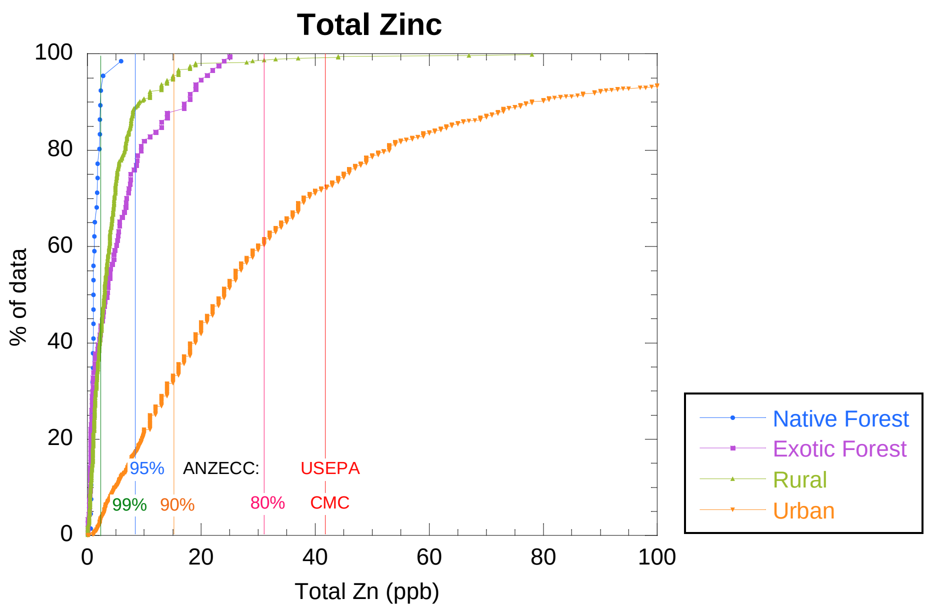


Figure 4-6 Probability plots for total zinc

4.2.3 Metals concentrations at individual sites within land use groupings

To show the effect of the dominant land use on stream metals concentrations at different sites within different land uses, the Auckland Council stream monitoring data were plotted for individual sites. These were arranged from catchments dominated by native forest through to exotic forest, rural and to urban. Within the urban grouping, sites are ordered by the **approximate** urban land use, based on values provided in Scarsbrook 2007 and approximations for the sites for which this data was not provided. Note that these per cent urban areas are based on land use in 2001/02 and will be out of date for any streams where there has been further urban development in the catchment after this date. The data are presented in box plots from Figure 4-7 to Figure 4-9.

The plots show a strong land use effect, with urban streams having markedly higher metals concentrations than streams in other land uses. Concentrations in urban streams often exceeded various levels of protection (ANZECC 2000 95%, 95%, 90%, 80%) and even acute toxicity guidelines (the US EPA CMC); US EPA 2007).

Interestingly, the range (10-90 percentile) of Cu concentrations in the urban sites are very tight within a site and across sites (Figure 4-7) despite broad differences in the per cent urban land use from around 4% for Otara (KH) to 99% for Pakuranga (BR). Because sites are simply ordered by approximate land use, it is not appropriate here to discuss possible relationships between Cu and per cent urban land use or thresholds of per cent land use, above which Cu concentrations increase. The agreement in Cu concentrations between urban sites suggests there may be a “typical” or default value for urban stream Cu concentration which would be useful for both developing and implementing attributes. With some further analysis, it may be simple to predict the likely Cu concentration (both median and 90th percentiles) in an urban stream with reasonable accuracy.

In contrast to Cu, Zn does not show the same “tightness” in the spread of concentrations between urban streams (Figure 4-8). Zn concentrations can be very different within an individual stream with order of magnitude differences in the interquartile range. Median concentrations also vary between urban stream sites, from 4 to 72 µg/L. This makes it difficult to predict the typical concentrations of Zn in a stream in the absence of data. It also means it may be difficult to predict what the maximum concentrations would be for a given stream, even when the median is known, as the variance differs from stream to stream. Additional data analyses would be required to determine whether there are other variables that can assist in explaining the variation between and within sites.

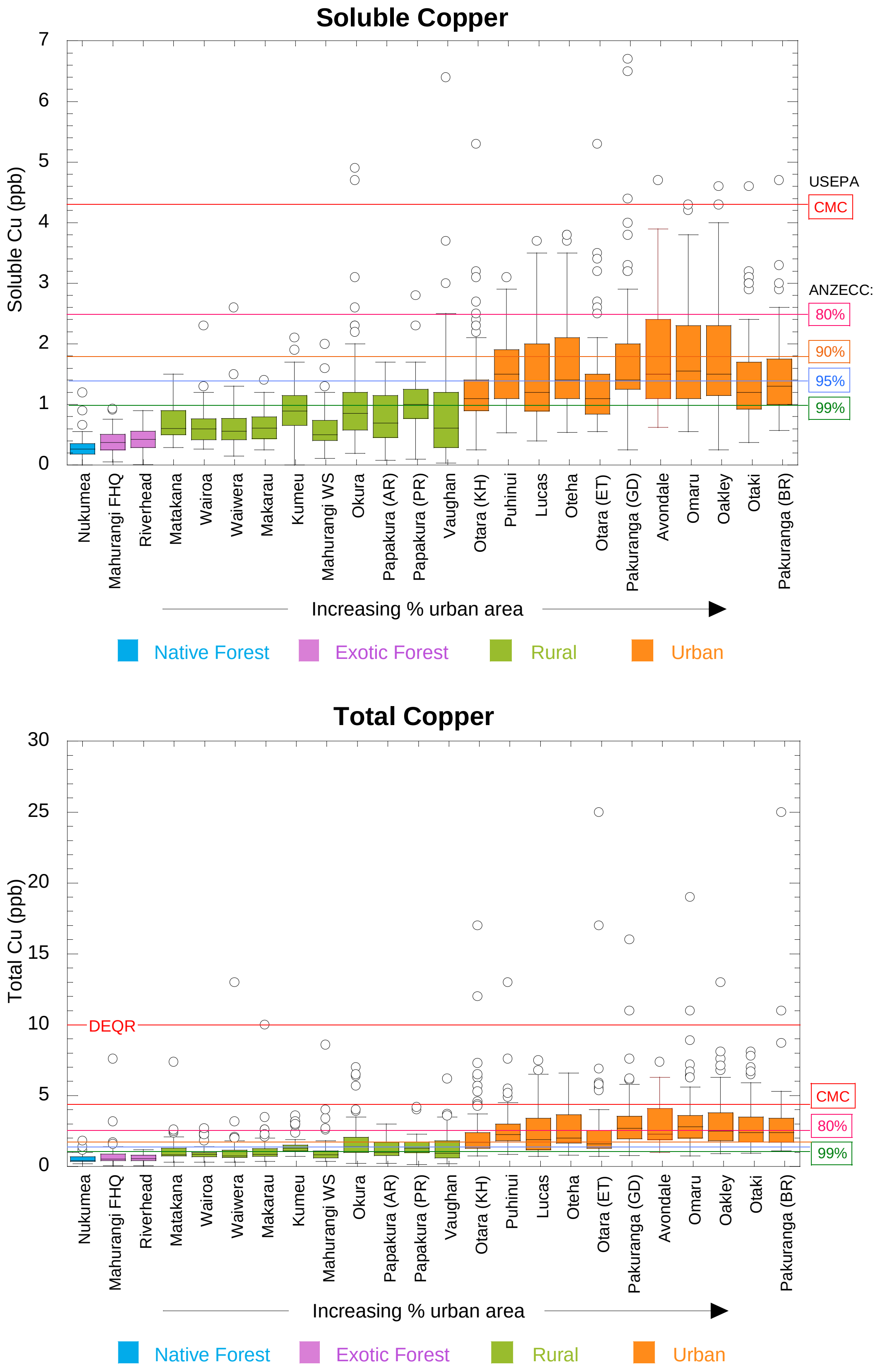


Figure 4-7 Box plots of metals by site, ordered by land use (approximate% urban) for soluble and total copper

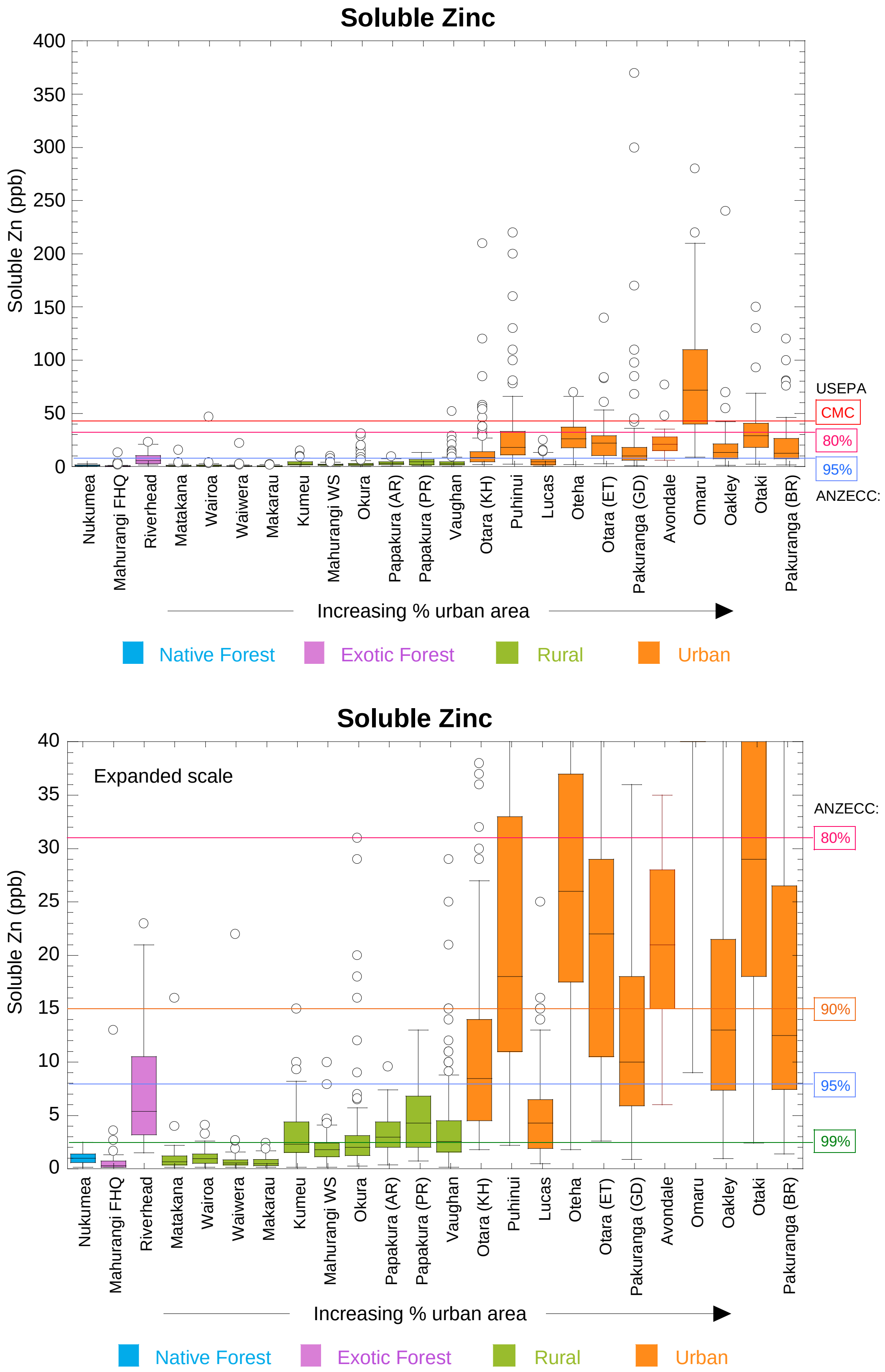


Figure 4-8 Box plots of metals by site, ordered by land use (approximate % urban) for soluble zinc. The lower plot has an expanded scale for better comparison with the more protective guideline values.

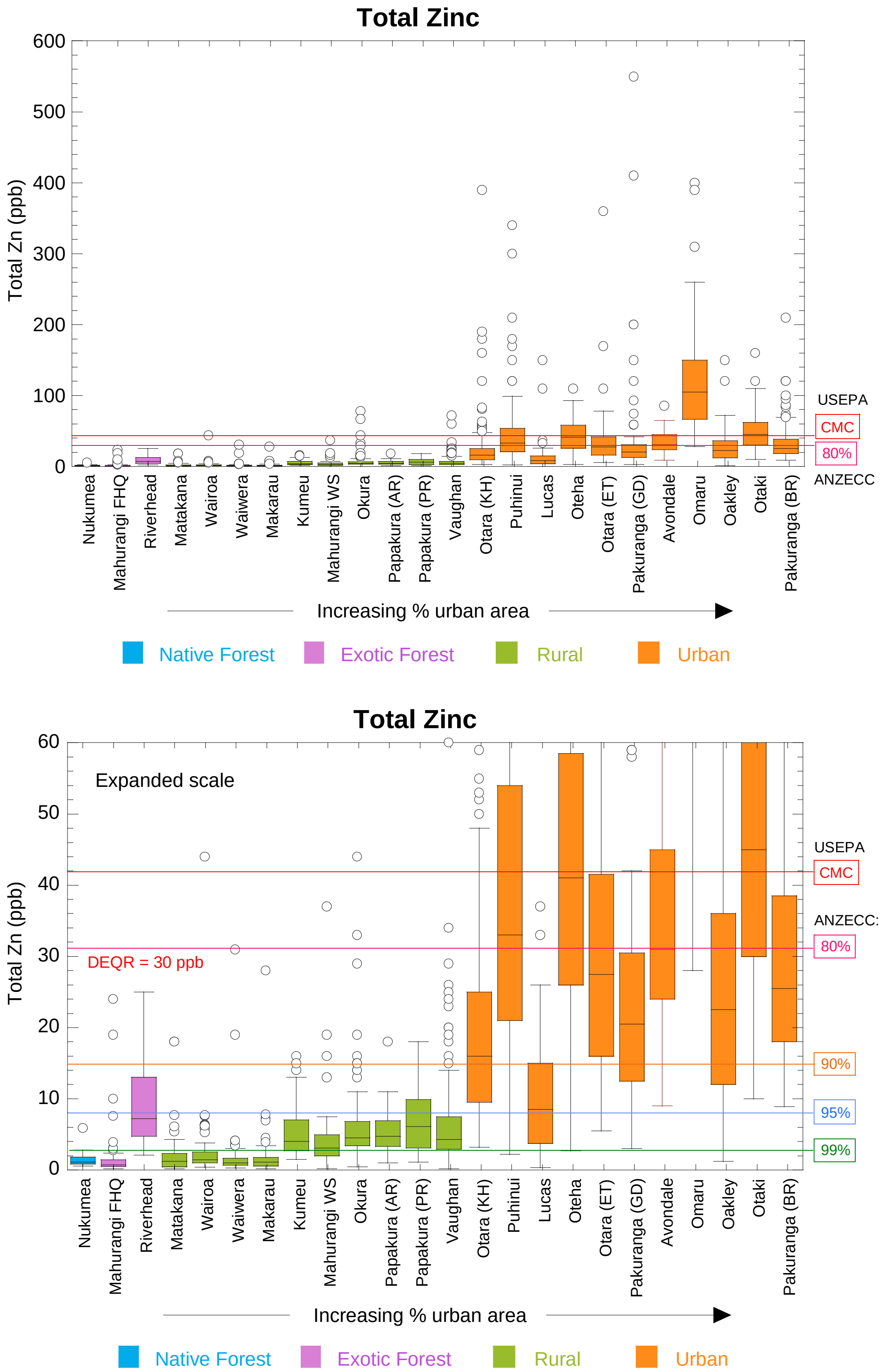


Figure 4-9 Box plots of metals by site, ordered by land use (approximate% urban) for total zinc. The lower plot has an expanded scale for better comparison with the more protective guideline values.

4.2.4 Relationships between quantitative estimates of urban land use and metals concentrations

The previous sections have illustrated the “urban effect” for metals, where Cu, and more particularly Zn, concentrations are higher in streams with urban development in the catchment. To further investigate the effect and whether there is a relationship between metal concentrations and urban land use, and to investigate whether there were well defined levels of urbanisation above which water quality guidelines are exceeded, quantitative data was obtained for each catchment upstream of each water quality monitoring site.

The relationships between quantitative estimates of land use (using CLM and LCDB4, see section 4.1.4) and soluble Cu and Zn concentrations were assessed through a LOWESS set to 0.3 span, modelled in R (R Developers Group, 2018) and the results are displayed in Figure 4-10 (for soluble Cu) and Figure 4-11 (for soluble Zn).

The relationships were explored for median and 95 percentile concentrations of long-term SoE instream concentrations for the period July 2005 to September 2014 (the latter to reflect “maximum” concentrations, without the most extreme outliers). The medians and 95 percentile concentrations were reasonably well correlated between sites for Cu, though less so for Zn – and therefore the land use vs concentration plots for medians and 95 percentiles were of similar shape for Cu (i.e., effect of land use was equivalent for general as well as more extreme metal concentrations instream).

Relationships between Cu and Zn concentrations and per cent urban land use showed generally increasing concentrations with increasing urban land use although concentrations of Cu did not appear to change much above about 30% urban land use (using either CLM or LCDB4 estimates). This “plateau” was less obvious for Zn. However, the data also showed very high variability (especially for Zn), indicating that factors other than land use contribute Zn to streams, which may limit general application of a simple relationship across Auckland catchments.

Although the LOWESS smoother line suggests a drop in metal concentrations for the sites with highest urban land use, it is not clear why this occurs. Variation in concentrations can be expected for any given per cent of urban land use due the range specific land uses (e.g., residential vs commercial), land covers (e.g., roofing types) and activities that could be occurring in the catchments of those sites. It may be simply an artefact of the high variability in concentrations in sites with urban land use of around 40% based on CLM and 60-80% based on LCDB4, compared to the variability for sites with higher urban land use. There is a possibility that it indicates a true decrease, for example due to stormwater treatment devices being prioritised to catchments with greater urban dominance, however this has not been explored.

For median concentrations (which might approximate “baseflow” conditions):

- Soluble Cu concentrations do not exceed the ANZECC 90% protection level (the 95% protection level is approached at about 30% urban cover – area by the CLM).
- Soluble Zn approaches the ANZECC 90% protection level at ca. 30-40% urban cover level (the 95% protection level is approached at about 15-20% urban cover).

For 95 percentile concentrations (which might approximate storm event concentrations):

- Cu concentrations do not exceed the USEPA CMC acute toxicity level. The ANZECC 80% protection guideline is exceeded above around 15% urban cover (area by the CLM).
- Zn concentrations exceed the USEPA CMC acute toxicity level and the ANZECC 80% protection guideline above ca.10-20% urban cover (CLM area).

Therefore, it appears that ANZECC 90% or 95% levels (for chronic base flow effects), and USEPA/ANZECC 80% (for 95 percentile “peak” concentration acute effects) are approached or exceeded at about 10-20% urban cover for Zn and about 15-30% for Cu.

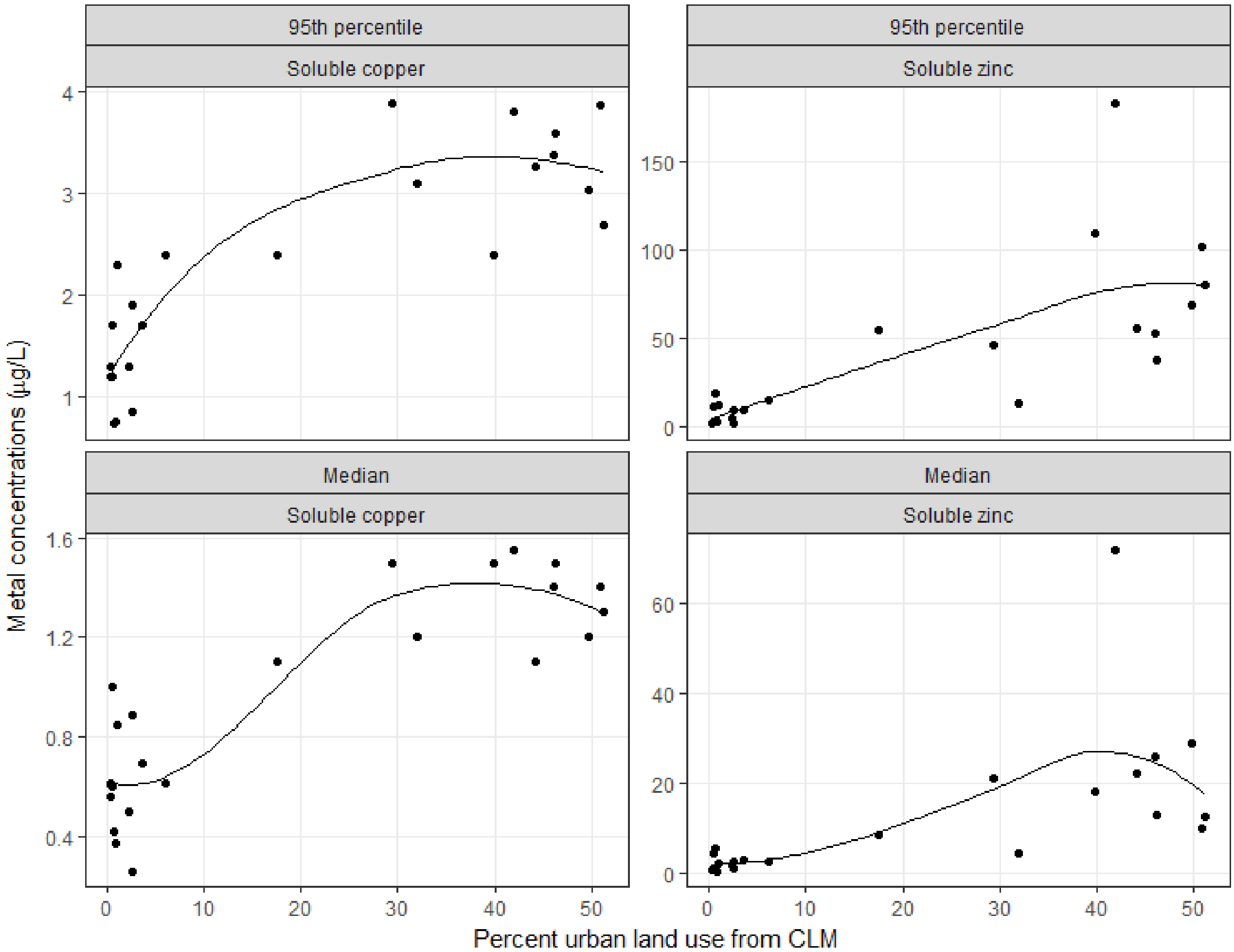


Figure 4-10 Soluble Cu and Zn versus % urban area (from the Contaminant Load Model – CLM). Plots have LOWESS smoother applied.

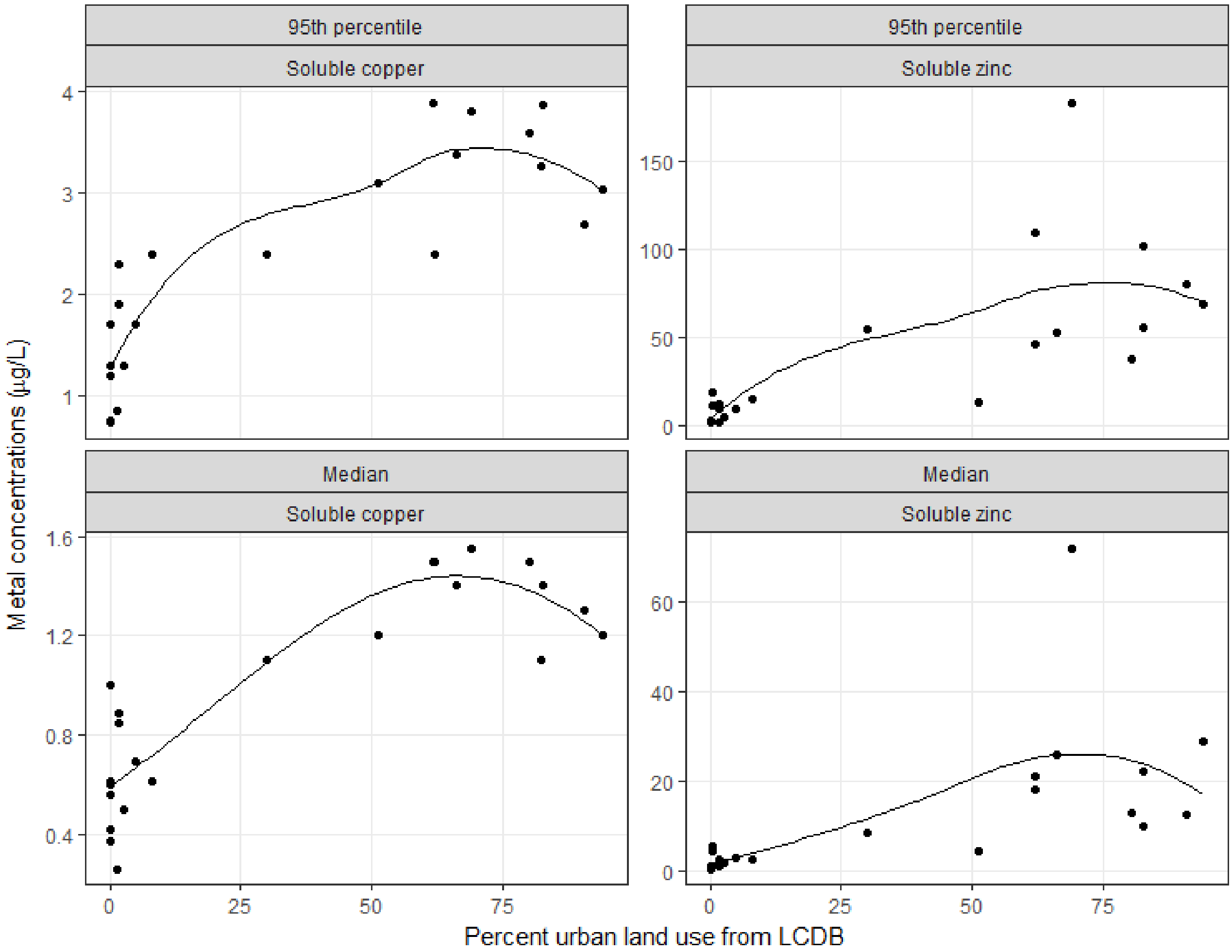


Figure 4-11 Soluble Cu and Zn versus % urban area from the Land Cover Data Base – LCDB. Note that the high outlier is from Omaru Creek – only for Zn, not Cu. Plots have LOWESS smoother applied.

4.3 Total/soluble concentration relationships

The ANZECC (2000) guidelines recommend a tiered approach, measuring first total metals and then, if this concentration is above the guideline, measuring dissolved metals. In this section the relationship between total and dissolved metals is briefly examined to assess whether the two forms are well enough correlated to predict one from the other. A more in-depth analysis is provided in Appendix B. Data from the Auckland Council SoE stream monitoring was again used for this analysis, using data from July 2005 to June 2014.

The relationship was investigated by linear regressions of total versus soluble metals, examining the slope and significance of the regression. Visual assessment of scatter plots was used as a check of data integrity (major outliers, (non)linearity). In addition total:soluble metals ratios calculated from each sample, for all streams and statistical summaries of medians (and means) and spread were calculated. These assessments were carried out for individual sites, by major land use groups (native forest, exotic forest, rural, and urban) and for all sites grouped.

There was a general relationship between the concentrations of total and soluble metals (Figure 4-12). Soluble concentrations generally increased with increase in total concentrations, although the relationship varied from site to site. For Zn, the range in regression slopes was 1-3.4 and for Cu the range was 1-3.0, excluding sites where the regression indicated higher soluble concentrations than total (which is not possible). There were a number of outliers but we have not assessed the reasons for this, which could be site-specific factors, related to flow or related to season.

When ratios of total to soluble were calculated for individual samples, the overall ratio for copper in urban streams (1.61) was very similar to that for zinc (1.58). There does not appear to be any clear difference in the ratios for streams with other land uses, as ratios for copper in native forest, exotic forest and rural streams were 1.7, 1.6 and 1.5 respectively and ratios for zinc were 1.4, 1.5 and 1.7 respectively. There is however there is limited data for the forested streams due to the fewer sites monitored.

The relationship is also important to understand when considering implications of the attribute tables to estuaries. In estuaries, the total load (and hence total concentrations) are important in terms of the build-up of metals in sediments. The detailed analysis of total/soluble in the Appendix will help to explore implications of freshwater management to estuary management. The soluble concentrations in attribute tables can be related to total concentrations through these ratios, to assist in understanding the total loads entering estuaries.

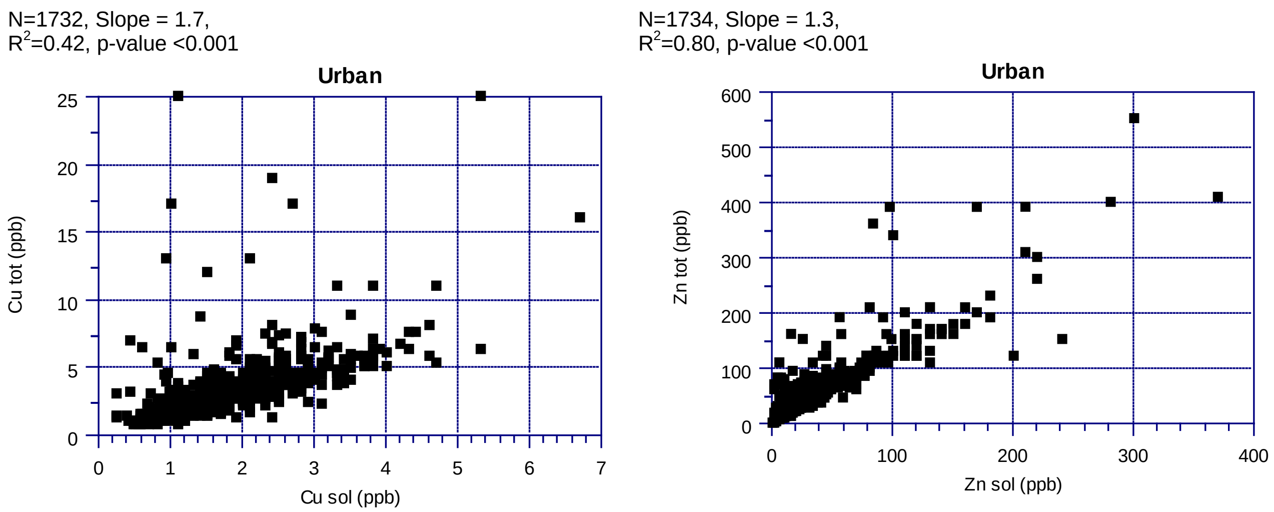


Figure 4-12 Scatter plots of total versus soluble copper and total versus soluble zinc. Data for urban streams only.

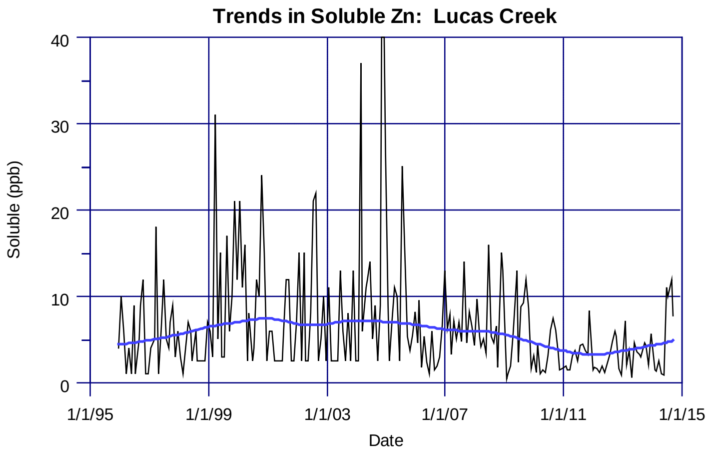
4.4 Temporal trends

This section briefly investigates and reviews trends in Cu and Zn in a subset of Auckland streams where monthly monitoring data was available for approximately 19 years, from December 1995 to September 2014. These four sites are Puhinui Stream, Lucas Creek, Oteha Stream, and Oakley Creek. Data were plotted over time for soluble Zn and Cu, however, Cu data were affected by higher detection limits before July 2005 and therefore no trend analysis was done for Cu. The other stream sites had records of nine years or less and have less power for detecting trends so trend analyses were not undertaken.

Trends were assessed using Time Trends software in 2014. The version used at that time replaced data below the detection limit with half of the detection limit (e.g., <1 µg/L would be replaced with 0.5 µg/L). Seasonal Kendall tests were used as sites showed seasonal differences. There were no adjustments for flow as flow data is not available for all of these sites at the same locations as the water quality data.

Two examples of trend plots (for Lucas and Oteha Streams) are shown in Figure 4-13. Other plots for soluble Zn and soluble Cu are found in Appendix C: Trend plots. Concentrations go up and down over time, but over the last approximately 10 years Zn concentrations have been generally stable or possibly decreasing at these sites. Apart from Oteha Stream (where concentrations approximately doubled from 1995 to 2001, then remained generally stable), there has been no major overall change in Zn over the past 19 years (trend statistics are summarised in Table 4-8). The increasing trend for Oteha Stream reflects the “step change” that occurred between 1995 and ca. 2001. Concentrations have remained generally stable since then (see plot).

Figure 4-13 Trends in soluble zinc for two streams with long term (19 years) data records.



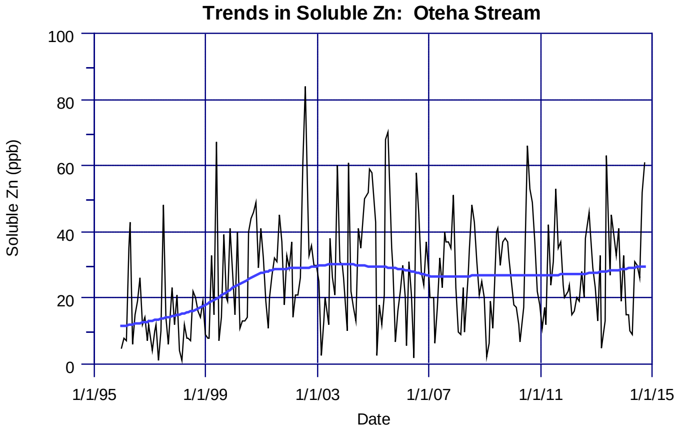


Table 4-8 Seasonal Mann Kendall trend test for soluble Zn. A significant decreasing trend was measured in Lucas Creek. The significant increasing trend in Oteha Stream was probably due to a “step change” increase that occurred between approximately 1995 and 2001.

Site	Trend		
	ug/L/year	% per year	P
Lucas	-0.114	-2.4	0.0031
Oakley	0.000	0.0	0.8560
Oteha	0.599	2.6	0.0006
Puhinui	-0.300	-1.4	0.1670

Temporal trends in dissolved copper and zinc in Auckland streams also have been assessed in two other reports (Gadd 2016; Buckthought & Neale (2016), each with different trend periods and slightly different methods, particularly for dealing with censored data. The results for the long-term trends for Lucas Creek, Oakley Creek, Oteha Stream and Puhinui Stream (Gadd 2016, Table 4-9) agree with those found in the above analysis (Table 4-8). However, trends over a shorter time period (e.g., 2008-2015) have shown different results, such as increasing trends in Zn in Puhinui Stream (Gadd 2016). The studies suggest that there may be more declining trends in Cu and Zn concentrations than increasing, but there are also many sites where the trends are not clear. This suggests that the current exceedances of guidelines with Cu and Zn are likely to continue into the future and that management will be required to protect ecosystem health.

Table 4-9 Summary of temporal trend results from other reports. Arrows represent trends established with confidence or statistical significance; question marks represent sites with indeterminant trends, dashes represent sites with non-significant trends.

	Trends 1996-2015[1]	Trends 2008-2015[1]		Trends 2005-2014[2]	
Site	Zn	Cu	Zn	Cu	Zn
Lucas Creek	↓	↓	↓	↓	↓
Oakley Creek	?	?	↓	↓	↓
Oteha Stream	↑	?	?	-	-
Puhinui Stream	↓	?	↑	-	-
Otara Creek (Kennel Hill)	NA	?	↓	-	↓
Otara Creek (East Tamaki)	NA	?	?	-	-
Pakuranga Creek (Greenmount)	NA	↓	?	-	-
Pakuranga Creek (Botany)	NA	?	?	-	-
Otaki Creek	NA	?	↓	-	-
Omaru Creek	NA	↓	?	-	-

Note: 1. Results directly from Gadd (2016), arrows represent trends established with confidence, question marks represent sites with indeterminant trends (insufficient data or change in trend direction).

2. Results from Buckthought & Neale (2016) Arrows represent trends that were significant at $p<0.05$ level, question marks represent trends that were not significant.

4.5 Twin Streams project

The Twin Streams project was initiated by Waitākere City Council (now part of Auckland Council) to evaluate the “Pressure, State, and Response” (PSR) framework for understanding and managing the effects of urbanisation on stream ecosystem health. The water quality monitoring component of the project (Diffuse Sources 2004, 2005) included measurement of dissolved Cu and Zn in streams waters from 15 sites in three major streams (Oratia, Opanuku, and Waikumete Streams), covering bush headwaters, rural areas, peri-urban (boundary between rural and urban), and urban locations (Figure 4-14). Sampling was conducted on six occasions at approximately monthly intervals over the 2003/4 summer (November to April) and on five occasions in summer 2005/6 (December to May – the April 2006 sampling was delayed by poor weather). Further information on sampling is given in Appendix E.

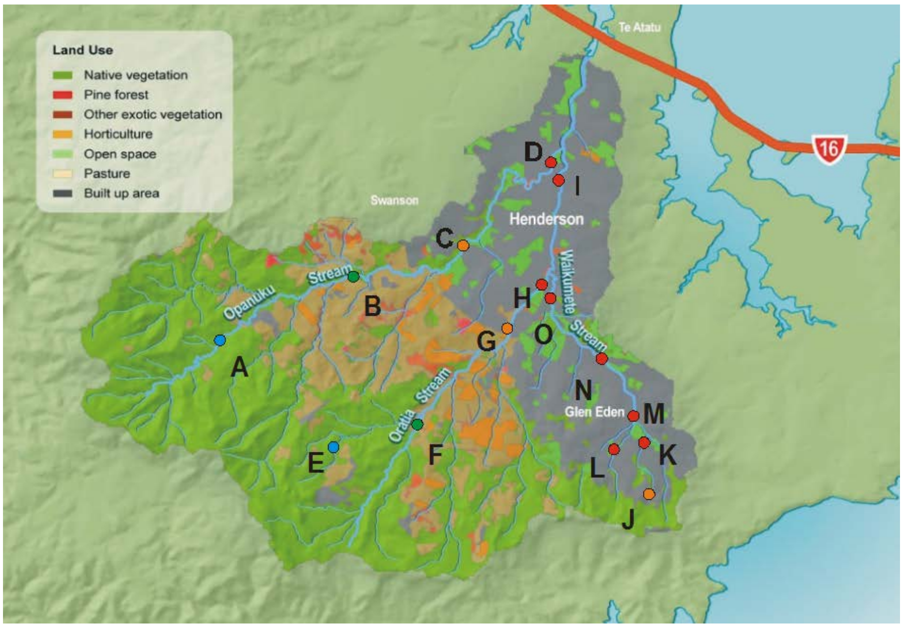


Figure 4-14 Water quality monitoring sites used in the Twin Streams project. Figure taken from Mills & Williamson (2008).

Water quality sampling was aimed at being undertaken in dry weather base flow conditions, at least two days after significant rainfall, to reduce data variability associated with high flow events. However, in practice this proved difficult to achieve on all occasions. Sampling occurred at base flow for all samplings except for three occasions when sampling was undertaken in the recession period following high flow (storm) events. The Twin Streams monitoring data therefore differ from the Auckland Council SoE stream data in that summer base flow monitoring was targeted and it is therefore biased to low flow events. This resulted in lower variability in the metal concentrations (e.g. compare Figure 4-16 and Figure 4-8).

The concentrations of dissolved Cu and Zn from the 2003/4 summer monitoring are shown in Figure 4-15 and Figure 4-16. Results from the 2005/6 summer monitoring showed a similar spatial pattern to those from 2003/4 (Appendix E), although 2005/6 levels were significantly higher at some sites. The high "outlier" levels occurred when the streams were receding following high flow events. This is indicative of the residual effects of high stormwater inflows from the preceding storms, including greater inflows from stormwater drainage systems in urban areas and ephemeral streams in rural areas, which would normally not be flowing during 'true' base flow, as well as greater inputs from groundwater.

Concentrations of Zn and Cu increased below the headwaters of the three stream systems, particularly for Zn below the urban fringe.

Copper levels also increased noticeably between sites F (rural) and G (peri-urban) in the Oratia Stream, possibly indicating a small effect of rural land use (e.g. residues from intensive horticulture in these catchments).

Highest Cu concentrations in 2005-6 were recorded during a recession event at the rural and peri-urban sites in the Oratia Stream (these data are not shown in Figure 4-15, which shows the data for 2003-4 monitoring). This may reflect Cu inputs from horticultural land in this stream catchment. Cu approached (and for some sites, exceeded) the USEPA criterion for acute toxicity at the rural and urban sites.

Median Cu and Zn concentrations were below the ANZECC 99% protection level at all the upper catchment reference sites (except site J on the Hibernia Stream), and at the rural sites. Median Cu and Zn concentrations were above ANZECC 95% protection trigger value at the urban sites.

Overall, the Twin Streams monitoring showed spatial changes in metals concentrations in relation to changing land use that were consistent with Auckland Council's long-term SoE stream monitoring. Baseflow concentrations of both metals were higher in urban streams than upstream in rural or native forest areas. The "urban effect" was less marked for Cu than Zn, possibly reflecting Cu use in horticulture in the rural areas of the Twin Streams catchment. Sampling after high flow events gave elevated metals concentrations, which is consistent with that seen in the Auckland Council SoE stream data (see section 5). The Twin Streams' data suggest that sensitive aquatic species are likely to be adversely affected by Cu and, more particularly Zn, even at base flows when stormwater inputs are relatively low. During higher flow events, acute toxicity levels are reached in the most impacted streams.

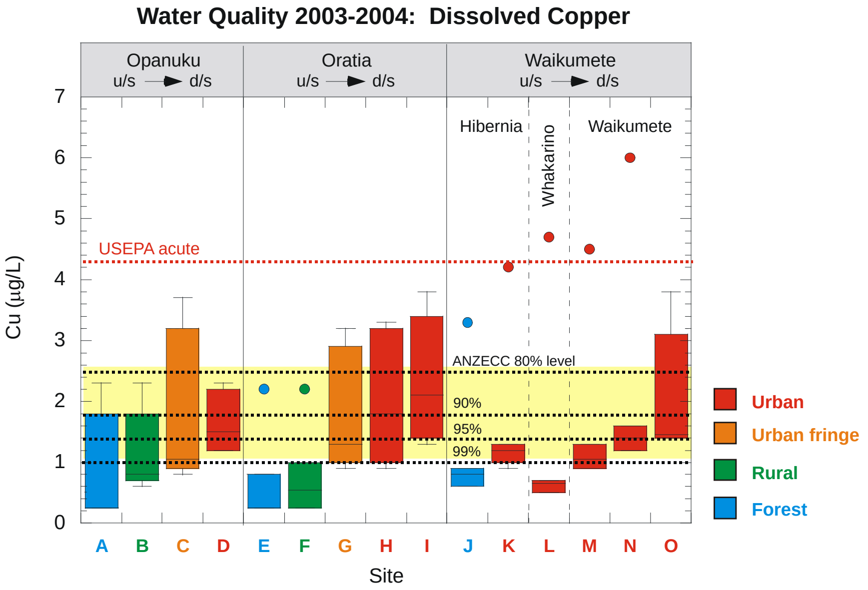


Figure 4-15 Concentrations of dissolved Cu from Twin Stream monitoring conducted over the summer of 2003/4 (adapted from Mills & Williamson 2008).

Sites are colour coded by land use: Blue (A, E, and J) are native forest headwater sites, green (B and F) are rural, orange (C and G) are urban fringe, and red sites (D, H, I, L, K, M, N, O) are urban. The yellow shaded area shows the range covered by the ANZECC guidelines for 80-99% protection levels.

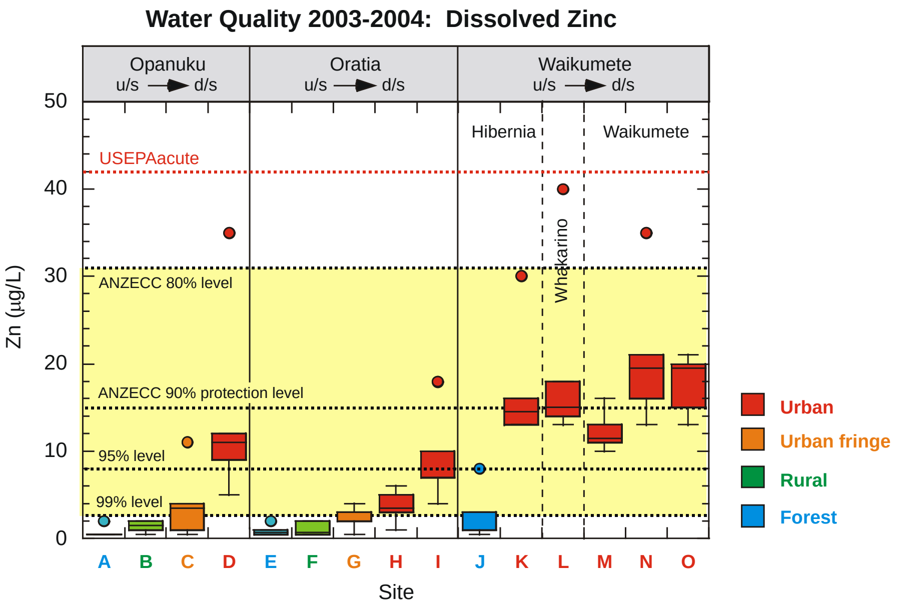


Figure 4-16 Concentrations of dissolved Zn from Twin Stream monitoring conducted over the summer of 2003/4 (adapted from Mills & Williamson 2008).

Sites are colour coded by land use: Blue (A, E, and J) are native forest headwater sites, green (B and F) are rural, orange (C and G) are urban fringe, and red sites (D, H, I, L, K, M, N, O) are urban. The yellow shaded area shows the range covered by the ANZECC guidelines for 80-99% protection levels.

4.6 Auckland data compared to other centres

Urban stream water quality data from AC, GWRC and Christchurch City Council were collated and compared in Gadd (2016). These data are used in Figure 4-17 and suggest that site median concentrations of soluble copper are similar in Auckland and Wellington, but that zinc concentrations are, on average, somewhat higher in Auckland than in Christchurch and Wellington. This may reflect differences in catchment land use, as although all are classified urban (based on ≥15% urban land use in the catchment), each will have differing percentages of urban land use, between 15 and 100%. Climate (e.g., total rainfall) and hydrological factors (e.g., influence of springs) may also affect the Cu and Zn concentrations. There are no Christchurch data available for soluble Cu as the majority were below detection limits. The data for Wellington and Christchurch also shows that (where data exists) Cu and Zn exceed ANZECC (2000) guidelines and confirms the need for Cu and Zn attributes in managing streams in urban centres outside of Auckland.

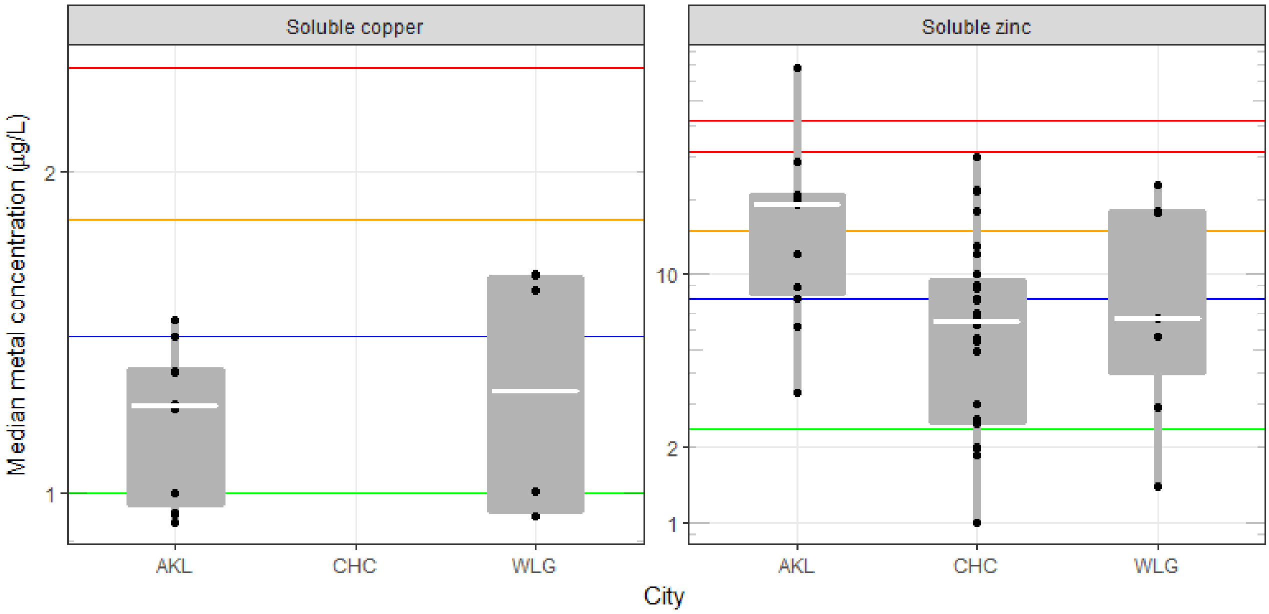


Figure 4-17 Median soluble copper and zinc concentrations (µg/L) at SoE sites in Auckland, Christchurch and Wellington. The coloured lines represent ANZECC (2000) 80%, 90%, 95% and 99% protection level guidelines.

4.7 Summary and recommendations

Auckland Council holds a relatively large data set of (and continues to monitor) Cu and Zn concentrations in streams through their SoE monitoring programme. This includes forested, rural and urban streams. The existing data indicate that many rural, exotic forest and native forest streams comply with existing water quality guidelines (except in upper quartiles of observed concentrations for Zn in exotic forest and Cu in rural classes), whereas urban streams frequently exceed the guidelines throughout their IQR, especially for Zn. For instance, all median total and nearly all median soluble Zn concentrations across urban streams, offered less than 80% community protection from chronic toxicity under ANZECC (2000). Overall, based on existing guidelines, Cu and Zn management is predominantly needed in urban streams.

This section has not investigated whether the data is of sufficient spatial representativeness to assess the current state of Cu and Zn in Auckland streams, nor whether the SoE data sufficiently represents all stream conditions (including high flow conditions). The first of these tasks may need to be done in the future as part of developing NPS-FM attributes. The second of these is investigated in the next section.

5 Relationships Between Metal Concentration and Flow

5.1 Scope

Stream water quality may vary considerably with flow. In urban catchments, storm events wash contaminants such as metals deposited on roads or roofs into receiving waters, thereby increasing contaminant concentrations in stream waters. Concentrations can rise with the “first flush” and then fall as the bulk of the deposited contaminants are washed away (Shamseldin 2011). The relationship between in-stream contaminant concentrations and rainfall/stream flow can be complex and may vary considerably at different locations within, and between, catchments.

This section investigates relationships between metal concentration and flow in order to provide a deeper understanding of the drivers and dynamics of metal concentrations in streams and to provide information to assist in determining the sample statistics most suitable for the attribute table.

This analysis requires flow data from the same time as the water quality samples are taken (or as close as possible to the same time). This is not available for all sites, as only a selection of the sites where water quality is monitored are also monitored for stream flow, limiting the analysis possible. To compensate for this, seasonal variation, and data from other sources is used to improve the understanding of metal concentrations at high flow versus baseflow.

5.2 Seasonal variation in metals concentrations: a surrogate for flow effects

As flows are not monitored at all SoE water quality monitoring sites, we examined the “seasonality” in the metals’ data. Seasonality – i.e. the variation in concentrations with “season” (e.g. seasons as in Winter, Spring etc, or as in months of the year) – was used as a surrogate for stream flow to test whether metals concentrations varied throughout the year in a pattern that was consistent with a probable stream flow effect (e.g. higher in winter than in summer).

The seasonality of the data was explored by plotting seasonal box plots and conducting a Kruskall-Wallis test (non-parametric ANOVA, using Time Trends software). In our initial assessment, all data from all sites was used (i.e., from 1995 to June 2014), rather than filtering for a limited time range, which would provide a more balanced data set with equal contributions to the data set being made from each site. Data were combined for all sites with the same land use grouping. In this assessment, some sites have more data than others and may therefore bias the overall picture obtained. Any further explorations of seasonality should refine the data set used to reduce the possibility of varying sample size bias.

Table 5-1 gives a summary of the Kruskal Wallis seasonality test results for Cu and Zn, with sites grouped by land use. Figure 5-1 shows examples of seasonal box plots. Other plots are found in Appendix D.

Table 5-1 Kruskall-Wallis test significance (p-values) for seasonality effects on Cu and Zn concentrations. Highlighted values are significant ($p<0.05$).

Land Use	Sol Zn	Tot Zn	Sol Cu	Tot Cu
native forest	0.191	0.547	0.303	0.788
exotic forest	0.548	0.242	0.162	0.198
rural	0.000	0.000	0.000	0.000
urban	0.000	0.000	0.000	0.000

Seasonality effects were apparent for soluble and total Cu and Zn for rural and urban streams. Exotic forest streams were also visually seasonal but the effect was not statistically significant, possibly due to lower sample number with only two sites in this category). There was no visual or statistically significant seasonal effect for the native forest category, which has only one site. In the urban and rural streams, metals concentrations were higher in winter, suggesting a “runoff” effect – where metals increase with increased rainfall. The seasonal effect was quite large in urban streams – e.g. median soluble Zn in February was 8.8 ppb, median in August was 28 ppb – a three-fold increase.

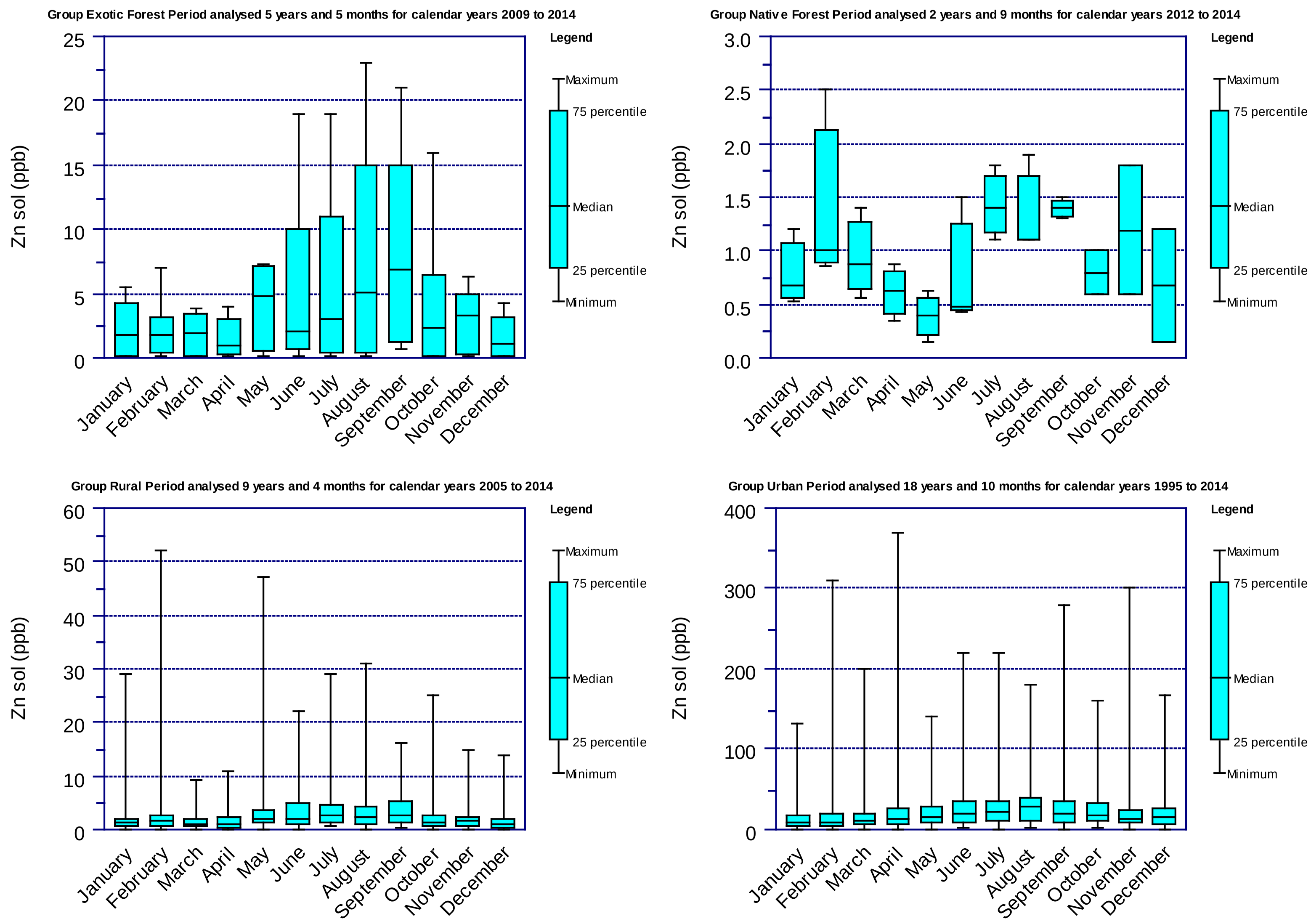


Figure 5-1 Seasonal box plots for soluble Zn, with streams grouped by land use (exotic forest, native forest, rural, and urban).

5.3 Concentration-flow relationships in state of the environment data

Soluble metal concentrations were plotted versus flow to examine the influence of flow on metal concentrations in Auckland streams. This analysis considered only the SoE sites where flow was measured at the same site as water quality (10 sites in total). Six of these sites are rural and exotic forest streams, and only the four urban sites (Puhinui, Oteha, Lucas and Otara Creek (Kennel Hill)) are included in this section. As several of these sites underwent urbanisation in the last 20-30 years, the monitoring periods were checked to ensure that this analysis only included data undertaken following urbanisation in the catchment (Table 5-2).

Table 5-2 Dates of monitoring and urbanisation in stream catchments where water quality and flow data co-exist.

Stream	Date metal monitoring began	Time of urbanisation
Puhinui	Dec-1995	Before 1996
Lucas Creek	Nov-2006	1996-2006
Oteha Stream	Dec-1995	1995-1997
Otara Creek (Kennel Hill)	Jul-2005	2003-2004

Flow data was obtained from Auckland Council for the same period as the metal monitoring data (Table 5-2). For this exploratory analysis, all data below the detection limit was removed as substituting data below detection with half of the detection limit could result to spurious results. Flow data was obtained for the date and time that water quality samples were collected, however times were not accurately recorded prior to 2005 and the flows selected may not represent the flow at the actual time of sampling. Metals data were plotted against flow data using R and linear regression models fitted based on log-transformed flow and concentration data.

The data, plotted in Figure 5-2, suggest a weak (e.g., r^2 <0.3) positive relationship between soluble Cu and flow for these sites, i.e., concentrations of Cu are generally higher with higher flows. This was similar for soluble zinc (Figure 5-3), except for the Otara Creek (Kennell Hill) site, where there was no apparent relationship. The scatter in these figures reflects that factors other than flow affect metal concentrations. For example, samples collected at later stages of a storm event often have lower concentrations than those near the start of the event, even at the same flow (the 'first flush' effect). Furthermore, samples collected on the rising limb of a peak are typically higher than those collected on the falling limb at the same flow (this is known as hysteresis, see Evans & Davies 1998). Antecedent conditions prior to a storm can also affect concentrations.

When guidelines are considered, it shows there is only a very weak relationship between flow and guideline exceedance. For both metals, guidelines are exceeded at both high flows and low flows, although there is more tendency to be below the guideline at lower flows.

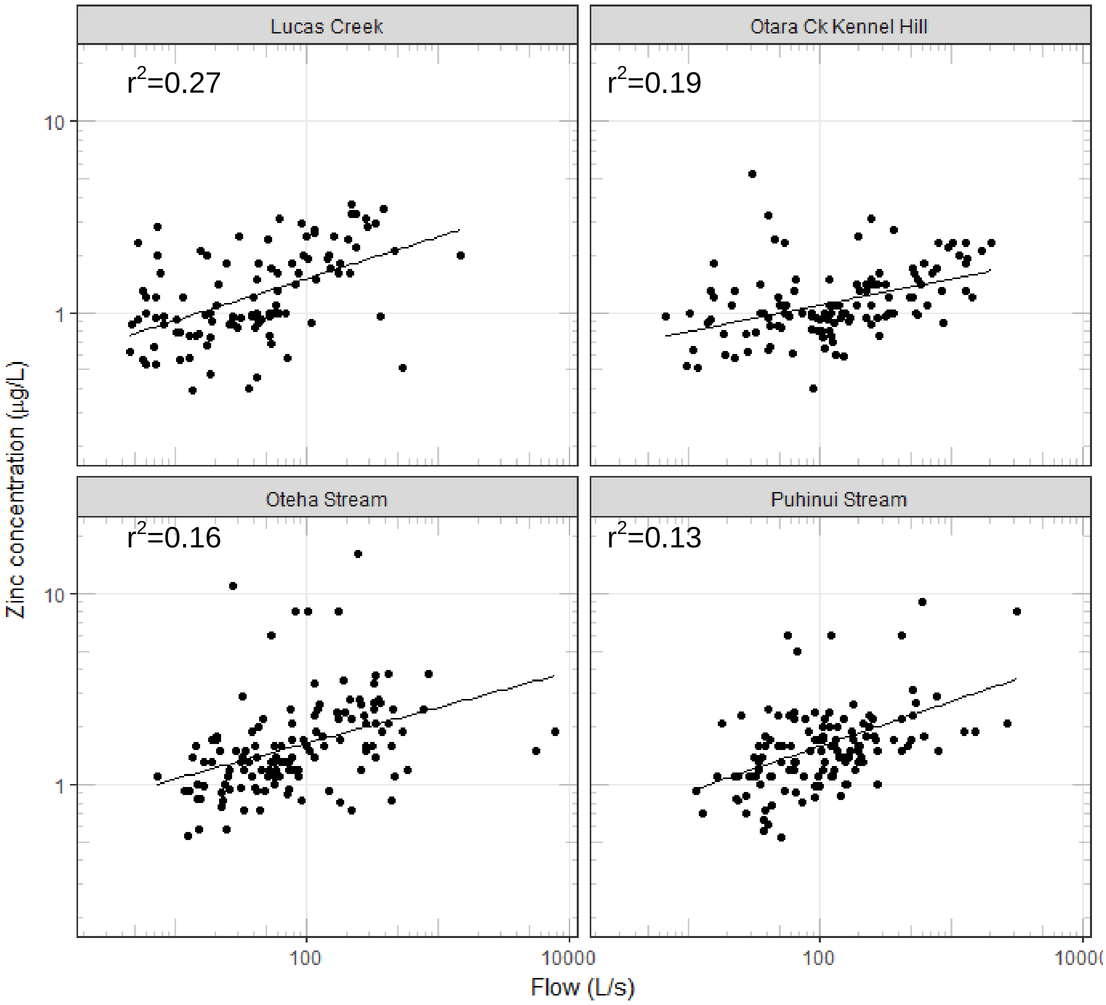


Figure 5-2 Flow (discharge, Q) versus soluble copper concentration relationships at the four urban sites with flow and metal data. Black line represents linear regression between concentration and flow, r^2 values for these regressions are shown on each plot. Note, a value of 300 µg/L for Puhinui Stream was included in this data set but is not shown in this plot.

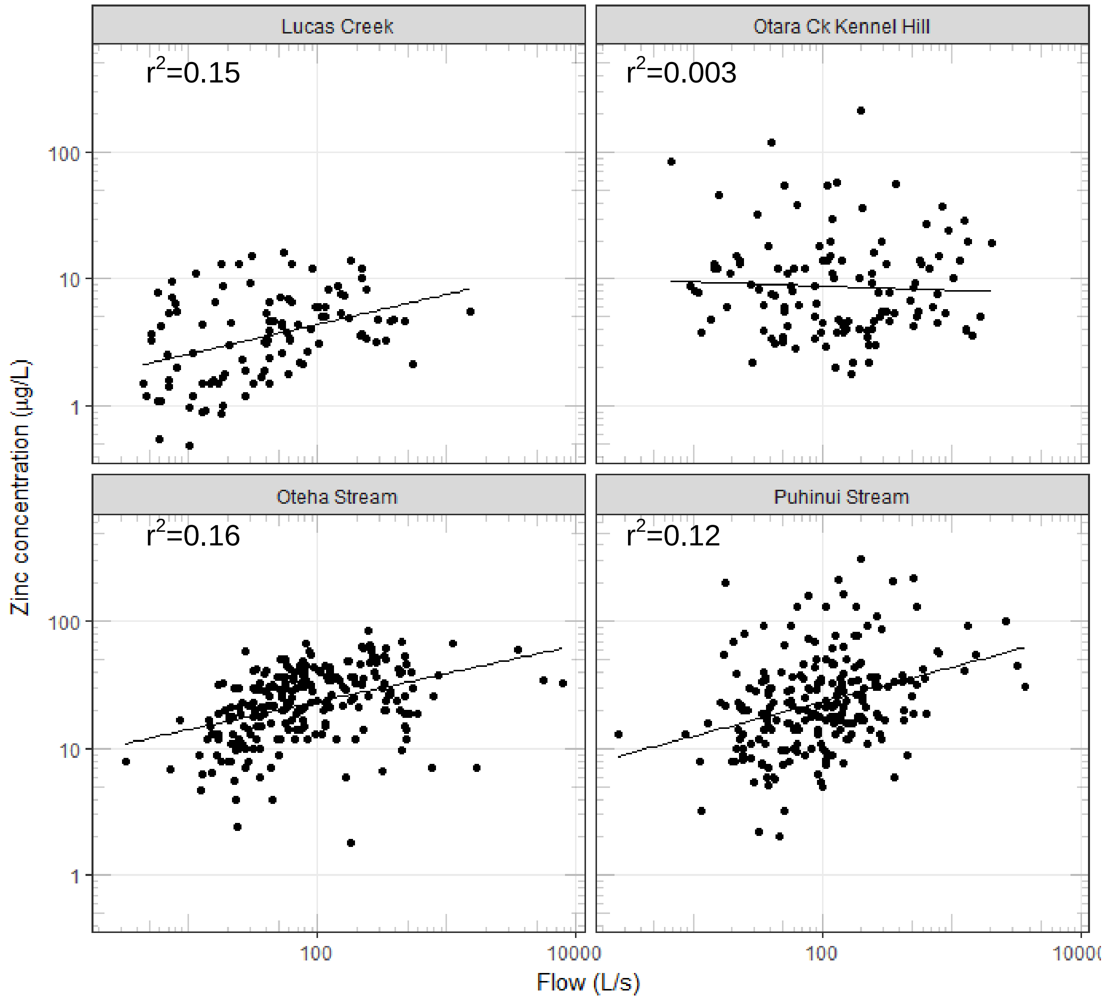


Figure 5-3 Flow (discharge, Q) versus soluble zinc concentration relationships at the four urban sites with flow and metal data. Black line represents linear regression between concentration and flow, r^2 values for these regressions are shown on each plot.

5.4 Hydrological representativeness of state of the environment monitoring

Stream SoE sites are sampled according to a schedule that does not necessarily avoid (or seek) varying magnitude of rain-runoff conditions. We analysed the data to see if it contained a comprehensive dataset, i.e., covered most flows including stormflows.

The plots above indicate that the sampling occurs during flows that range over more than three orders of magnitude (i.e., 1-1000 L/s) for most sites, with occasional sampling at 1000 to 5000 L/s, depending on stream. When compared to flow duration curves for each site (Figure 5-4), this indicates the SoE programme is not only sampling baseflow conditions, but regularly samples flows that occur up to between 88 and 92% of the time, with occasional sampling of the high flow events that occur less than 10% of the time (e.g., over 1000 L/s).

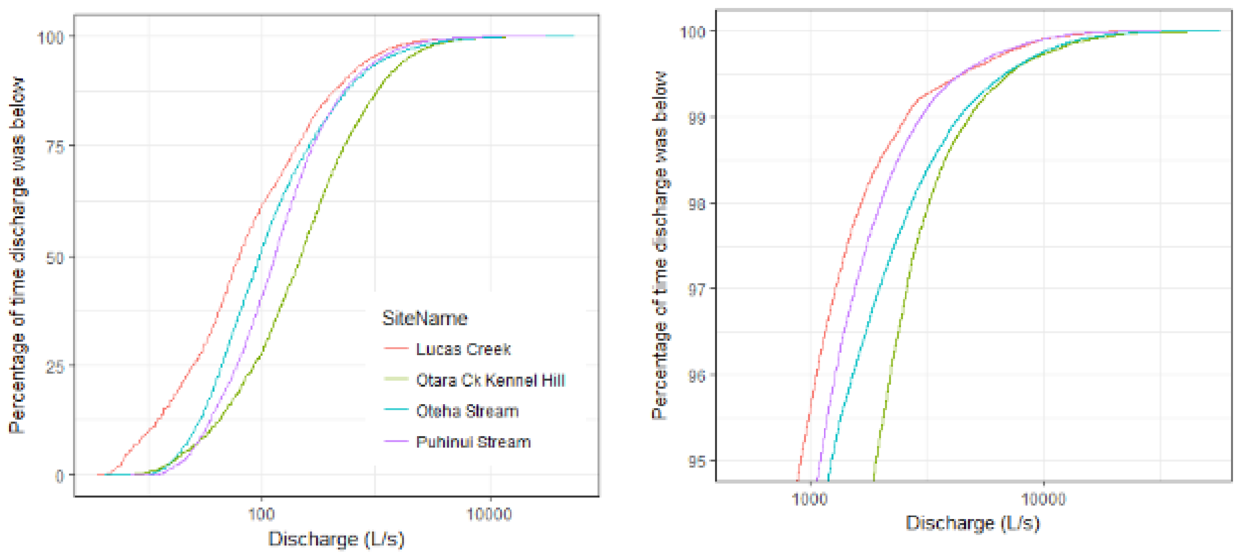


Figure 5-4 Flow duration curves for Lucas Creek, Otara Creek (Kennel Hill), Oteha Stream and Puhinui Stream, showing complete curve and close-up of flows > 1000 L/s.

A comparison of the flow duration curve for times when water quality samples were collected, with the curve for the complete flow record (Figure 5-5) indicates that although higher flows are at times sampled, there is an overall bias towards sampling during lower flows. This is shown by the location of the curve for sampling events to the left of the full flow record (i.e. at lower flows). For example, approximately 67% of samples from Oteha Stream are taken at 100 L/s or less, however flows <100 L/s occur only ~50% of the time, so these lower flows are slightly over-represented in the monitoring record.

Because there is a positive relationship (albeit weak for some sites) between metal concentrations and flow, the significance of this sampling bias is that the sampled distribution of concentrations may not be fully representative of the true distribution. However, as the difference between the two flow records is only slight, and the relationship between flow and concentration also appears to be weak, it is likely that this does not result in a substantial bias in the results obtained through the SoE monitoring.

One aspect that remains unresolved is the timing of the sampling: whether on the rising limb or flow peak, or during the flow recession. This is expected to influence the metal concentrations as first-flush stormwater frequently has higher metal concentrations which would result in higher concentrations on the rising limb or flow peaks. It is possible that the sampling at higher flows was during recession flows and therefore missed the peak metal concentrations.

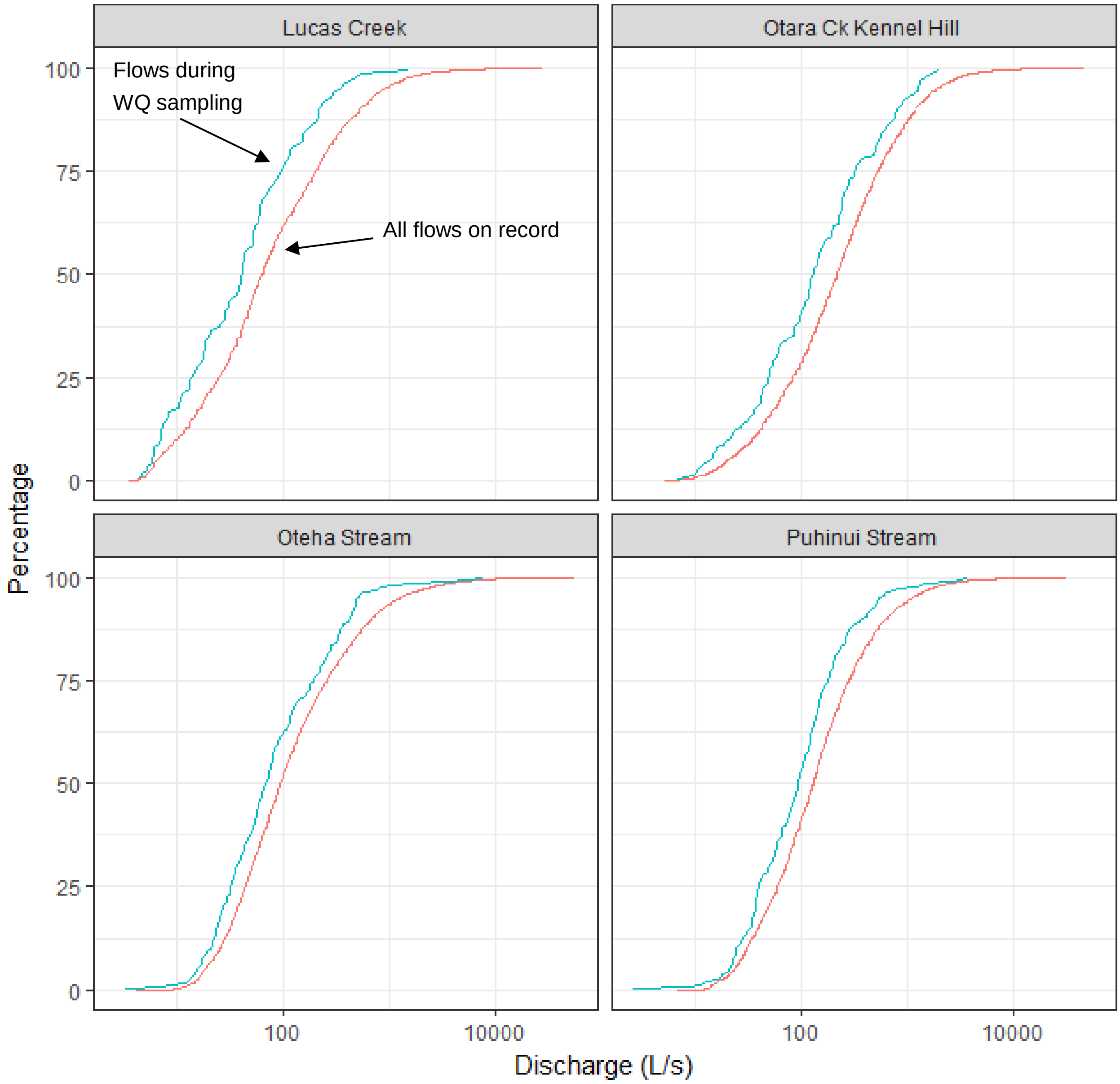


Figure 5-5 Flow duration curves for Lucas Creek, Otara Creek (Kennel Hill), Oteha Stream and Puhinui Stream for all flows and during water quality sampling events.

5.5 Comparison of baseflow and storm flow metal concentrations

To further understand the importance of storm flows (and whether it is important for the SoE data to represent all stream conditions including storm flows), we examined data collected under baseflow and storm flow conditions.

A first look at this used the ‘Urban Runoff Quality Information System’ (URQIS)[5], a comprehensive database of concentrations of Cu and Zn in New Zealand urban streams and stormwater although at this stage the database does not include SoE stream monitoring data. A brief analysis of this data suggests that both dissolved Cu and Zn concentrations are higher during storm events than they are under baseflow conditions. However, in many cases differing sites were sampled for the baseflow and storm events. This analysis provides only a rough comparison, indicating there is a need for analysis of data from sites with sampling across flows.

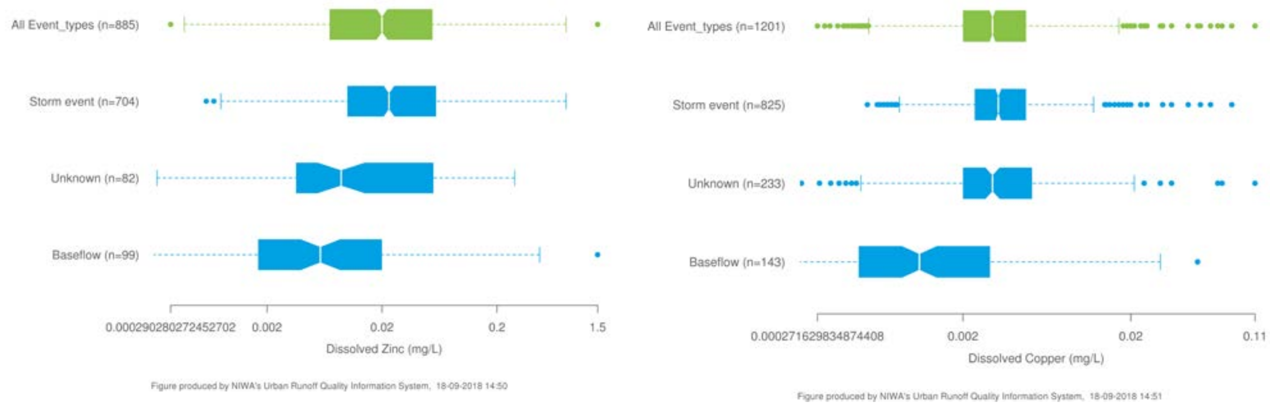


Figure 5-6 Soluble zinc and copper concentrations measured under storm events, under baseflow conditions and under unknown flow conditions. Data are from the URQIS database.

5.5.1 Comparison of storm flow and SoE monitoring

SoE stream water quality summary statistics were compared with storm flow summary statistics from five urban streams (at six sites) in studies conducted by NIWA for Auckland City Council (Reed & Timperley 2004, Moores et al. 2006, Gadd et al. 2009). The comparison is shown in Figure 5-7.

It is important to consider what is being compared here. The SoE stream sites were sampled routinely (regularly on a monthly basis), presumably rarely sampling peak flows, but probably occasionally encountering recession flows. The NIWA stormflows study focused on storms, and sampling was triggered by a rise in stage. Therefore, the two datasets are sampling mostly very different hydrological conditions. However, there is also no overlap in the sites and some of the differences may be due to catchment and site characteristics rather than flow- and sampling considerations. Note that although there are sites in Oakley Creek for both the SoE programme and the storm flow studies, these are different sites.

The data showed the stormflow sites had consistently higher, but not much higher, concentrations of dissolved Cu than at the SoE sites sampled less intensively for storms, with concentrations covering a relatively narrow range (90th percentiles were approximately 2-3 ppb in the SoE sites

[5] http://urqis.niwa.co.nz

and 4-8 ppb in the stormflow sites, Figure 5-7). Dissolved Zn concentrations were much more variable (note log scale on plot, Figure 5-7), both within and between sites, with markedly higher concentrations (and ranges) found at two sites (Omaru and Motions). Some of the stormflow sites (Meadowbank, Oakley and Blockhouse Bay) were comparable with the SoE sites, and did not show greatly elevated concentrations during stormflows, whereas the Wolverton and Meola sites showed more elevated concentrations during stormflows. Overall, the dissolved Zn results showed variable effects of stormflow, with site-to-site variability potentially being the dominant feature of the data. This is consistent with the weak, and scattered relationship between metal concentrations and flow observed at selected SoE sites as described in section 5.3 (Figs. 4-2 and 4-3).

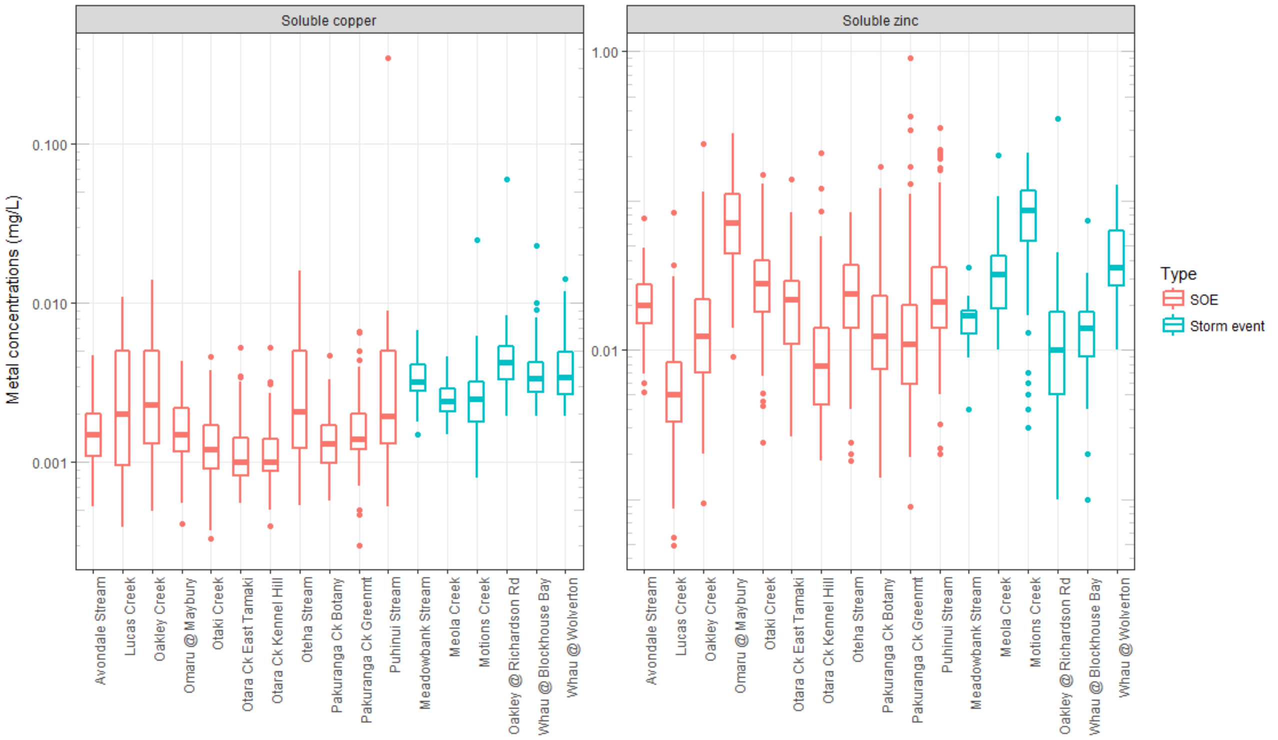


Figure 5-7 Dissolved copper and zinc distributions for urban SoE sites and storm sites. Eleven SoE sites on left, six storm flow stream sites on right of plot.

5.5.2 Auckland streams

Data for streams that were sampled in both wet weather and dry weather (baseflow) would provide a clearer indication of the effect of storms on metal concentrations. Sampling of two dry weather flows and two wet weather flows in 16 small Auckland streams in 2002 showed higher concentrations for soluble Cu and Zn in wet weather (Webster et al. 2004, summarized in Griffiths & Timperley 2005 and Mills & Williamson 2008). A graphical summary of these results is shown in Figure 5-8. The comparison to SoE sampling indicates that concentrations as high as these have been measured in the SoE monitoring programme. However, it is not possible to tell from this whether such concentrations in the SoE monitoring are associated with storm flows or are simply due to different site and catchment characteristics.

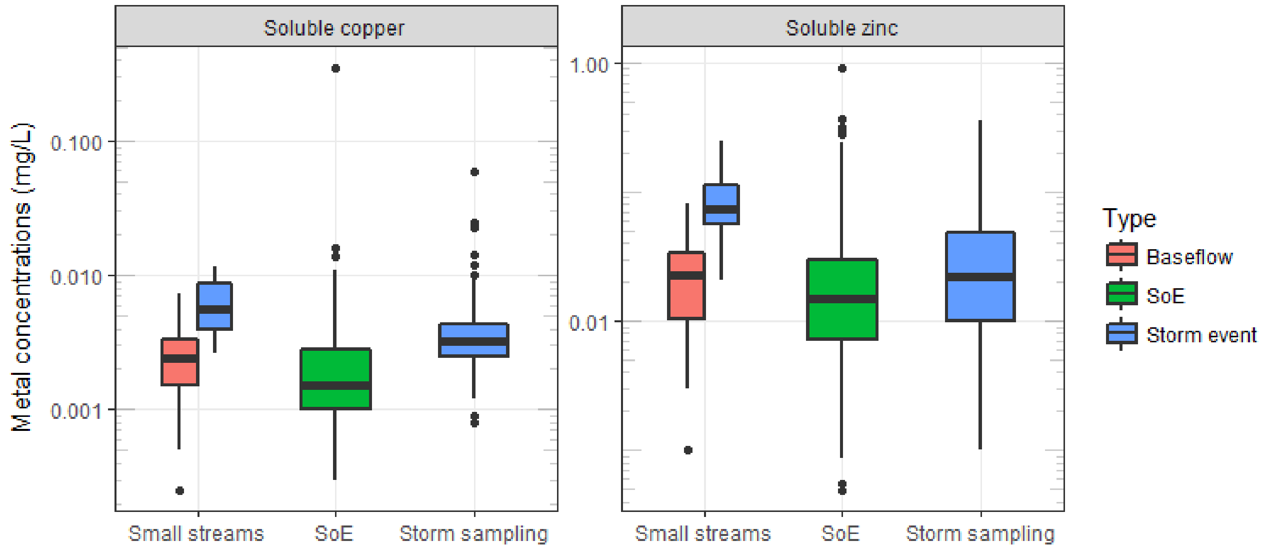


Figure 5-8 Base flow and storm comparisons for soluble Cu and Zn in 16 small Auckland streams compared to SoE sampling and storm event sampling at various streams (11 for SoE, 6 for storm sampling, sites as in Figure 4-7)..

5.5.3 Comparison of low flow and storm flow samples in Christchurch

Dissolved concentrations of Cu and Zn also showed similar variable behaviour at seven sites on Haytons Stream in Christchurch (Moores et al. 2009). Comparisons were made between three dry weather samples and one wet weather samples, and time-proportional samples collected over one storm event. The data, which are summarised in Figure 5-9 and Figure 5-10 (from Moores et al. 2009), showed:

- There were slightly higher dissolved Cu concentrations at most sites during wet weather sampling.
- At most sites there were no, or minor, differences between dry and wet weather concentrations of dissolved or total Zn.
- Dissolved Zn concentrations did not demonstrate a consistent pattern in the samples collected over each storm.

Further sampling at one site in the catchment, Gerald Connolly Place (identified as HAS-GCP in Figure 5-9 and Figure 5-10) was undertaken by the University of Canterbury using autosamplers to collect samples hourly. This sampling illustrated in Figure 5-11 and Figure 5-12 showed that the Cu and Zn concentrations were generally higher during storm flows than during baseflow, though this was not always the case (see copper, baseflow 3 and stormflow 1 in Figure 5-12). The concentrations receded throughout some storm events, but not all.

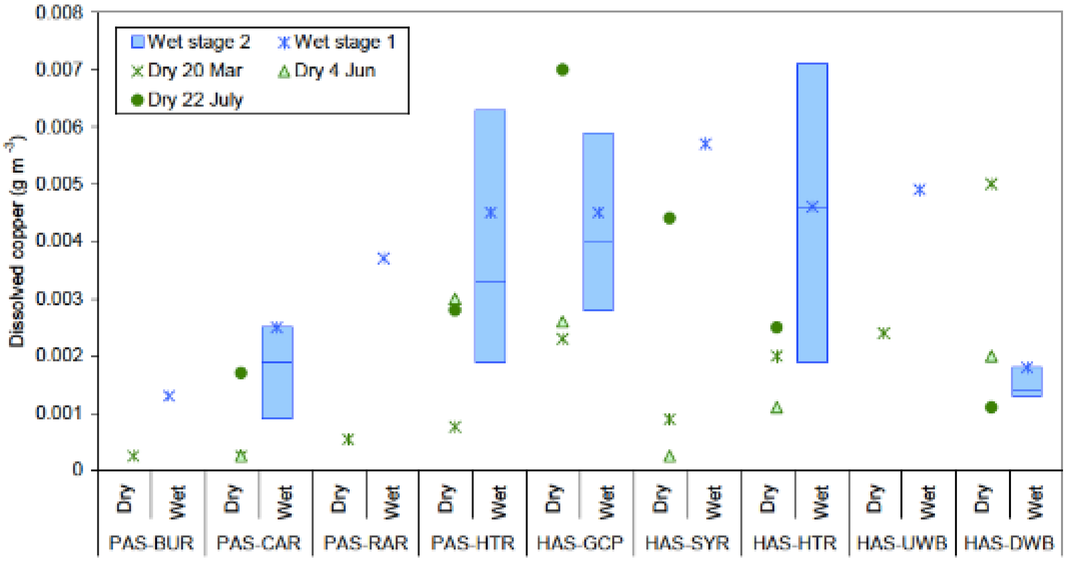


Figure 5-9 Dissolved copper concentrations at nine sites in Haytons Stream catchment (Moores et al. 2009, Figure 24).

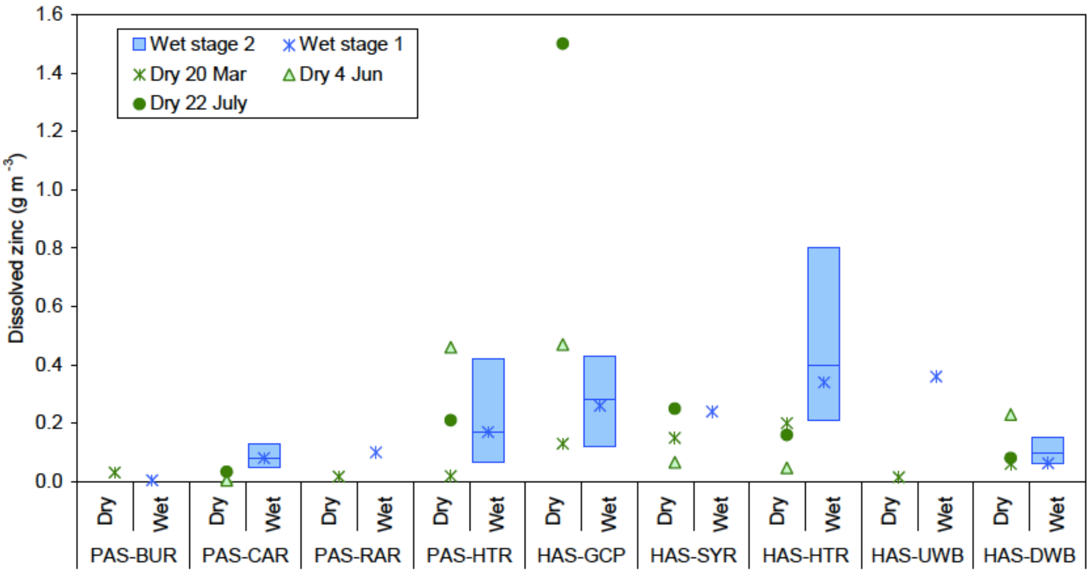


Figure 5-10 Dissolved zinc concentrations at nine sites in Haytons Stream catchment (Moores et al. 2009, Figure 24).

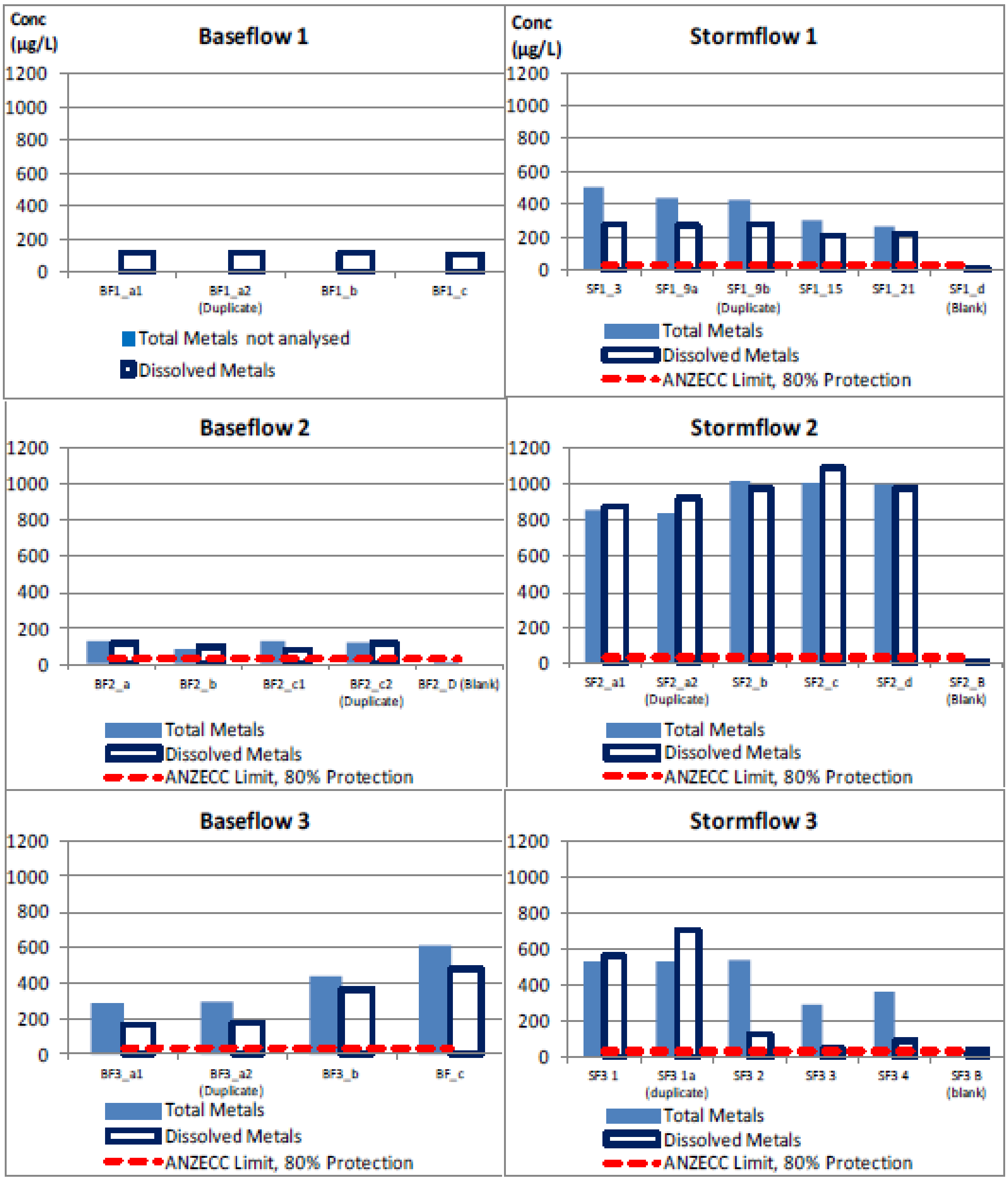


Figure 5-11 Total and dissolved zinc concentrations in Haytons Stream at Gerald Connolly Place during baseflow and storm flow sampling occasions (O'Sullivan & Charters 2013).

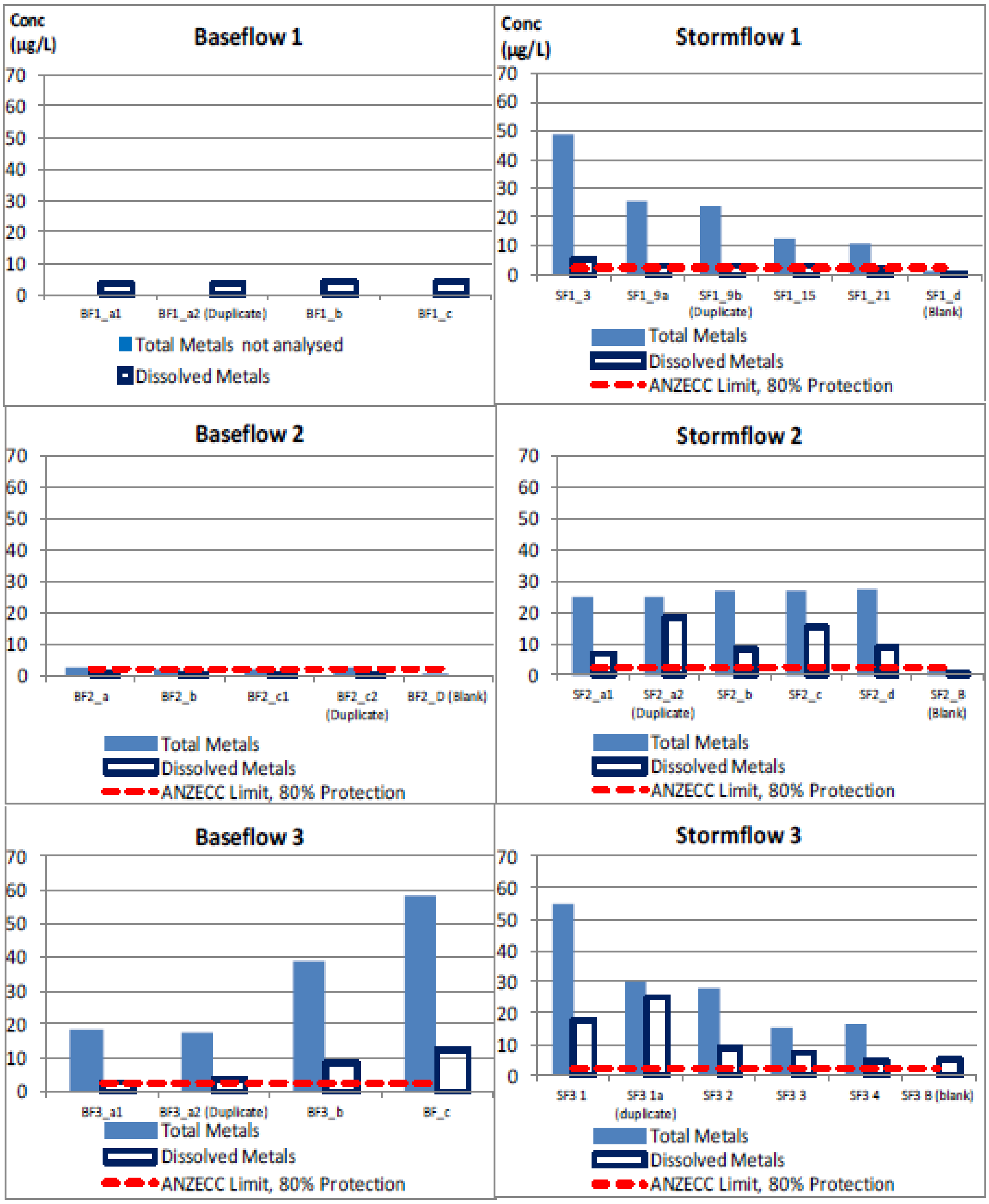


Figure 5-12 Total and dissolved copper concentrations in Haytons Stream at Gerald Connolly Place during baseflow and storm flow sampling occasions (O'Sullivan & Charters 2013).

5.6 Summary and recommendations

There appears to be a weak relationship between stream flow and metal concentrations, with higher concentrations at higher flows. This is shown for the few urban sites where flow and water quality data are measured at the same site, and also as suggested from the seasonality effects that indicate generally higher metal concentrations in winter, when stream flows are also likely to be higher.

In other studies in Auckland and across NZ, samples collected under storm flows typically show higher metal concentrations than those collected under baseflow. However, this is not always the case, and further data analysis would be useful to examine whether storm flows (and complete storm events, capturing rising, falling, and peak stages of the storm) must be sampled to characterise the maximum metal concentrations.

It is not clear whether the SoE monitoring programme sufficiently represents all stream conditions, particularly peak flows and rising limbs. If these conditions are not sampled, the programme may be missing the peak metal concentrations. Further analysis of the hydrological record at the time of sampling could help to determine this, however there are only suitable flow records for 4 of the 11 urban stream sites.

6 Overall Summary and Recommendations

6.1 Summary of this discussion paper

The work described in this report was primarily undertaken in 2015 after a workshop between Auckland Council Greater Wellington Regional Council and Environment Canterbury staff and research providers. Further analyses of metal concentrations and flow were undertaken in 2016/2017. The development of attribute tables remains incomplete. This report incorporates both these phases of work in a publicly available document to enable other organisations to use the analyses undertaken and information compiled and proceed with the tasks identified as required for attribute development.

Cu and Zn cause toxicity to aquatic life and there are water quality guidelines for Cu and Zn to protect from chronic exposure (ANZECC 2000; US EPA 1995; 2007) and from acute exposure (US EPA 1995; 2007). These guidelines, as reviewed in this document, could be used to develop attribute tables using the various levels of protection provided in ANZECC and the acute thresholds from US EPA. The ANZECC (2000) guidelines are currently being updated and the revised guidelines (due 2019) are expected to incorporate additional toxicity modifying factors. There are no New Zealand acute guidelines and there are short-comings of the US guidelines as they do not include any New Zealand native species.

To date, attribute tables for toxicants in NOF use a two-number system, with an “average” condition and a “maximum” condition. Strawman attribute tables were developed for Cu and Zn aligning with this framework. When tested based on SoE monitoring data from 2005 to 2014, urban streams overall achieved either a ‘C’ or ‘D’ state for Cu (depending on whether 90th or 95th percentile or maximum were compared) and a ‘D’ state for zinc (irrespective of statistic). When individual streams were compared, all urban streams achieved a ‘C’ state for Cu and most a ‘D’ state for Zn, with only 2 out of 11 urban streams meeting the strawman national bottom line for Zn. The choice of statistic for the “maximum” condition has a clear effect on the grading for Cu and some effect for Zn.

The analysis of Auckland freshwater stream data from Auckland Council state of the environment (SoE) monitoring sites (based on data 2005 to 2014) and from a catchment study in the Twin Streams (Waitākere) catchment shows the strong effect of land use on Cu and Zn concentrations, with higher concentrations in streams with urban catchments compared to rural and forested catchments. Cu concentrations are fairly similar between streams with 30% or more urban land use in the catchment, whereas Zn concentrations are more variable, both between sites and within a site. Cu concentrations in Auckland streams are very similar to those in Wellington whereas Zn concentrations may be somewhat higher in Auckland than in Wellington and Christchurch. Cu and Zn also exceed guidelines in streams in those cities indicating that national attributes will be useful for management in these urban centres. There are no clear downward trends in the Cu and Zn concentrations in the Auckland streams, suggesting that the need for management to protect ecosystem health will continue.

The SoE monitoring data shows seasonal variation in Cu and Zn concentrations. Analysis at sites with flow data suggests that there is a positive but weak relationship between stream flow and Cu and Zn concentrations. This is supported by data from other studies and other urban centres, showing higher concentrations in samples collected under storm flows compared to those collected under baseflow. This has implications for the use of an acute threshold or a maximum condition in the development of attribute tables, especially whether a maximum is overly conservative given existing acute toxicity testing is from exposures in the order of days whereas monthly grab samples might record maxima lasting hours.

6.2 Progress on principles for attribute development

The table below links the work completed in this project to the process for developing NPS-FM attributes, as defined using the following NOF five principles or requirements (Section 0). There are still a number of items remaining that need to be resolved for the development of an attribute to be rigorous and to the standards expected of the NOF.

1. Link to the national value	
Is the attribute required to support the value? Does the attribute represent the value?	The attributes are accepted as important aspects of ecosystem health
2. Measurement and band thresholds	
Are there established protocols for measurement of the attribute?	Yes there are, although this has not been reviewed in this report.
Do experts agree on the summary statistic and associated time period?	There is still much work to do on the summary statistics and associated time period; and the type of monitoring required to measure these, principally for the 'maximum' condition statistic with the median generally agreed a sensible measure.
Do experts agree on thresholds for the numerical bands and associated band descriptors?	ANZECC (2000) guidelines are under review. There are no New Zealand acute thresholds at present.

3. Relationship to limits and management	
Do we know what to do to manage this attribute?	This is widely understood.
Do we understand the drivers associated with the attribute?	The main driver is urbanisation however, relationships with land use and flow are complex.
Do quantitative relationships link the attribute state to resource use limits and/or management interventions?	This is broadly understood.
4. Evaluation of current state of the attribute on a national scale	
What do we know about the current state of the attribute at a national scale?	There is a good understanding of Cu and Zn on the national scale for urban streams. Less is known on Cu and Zn in other land uses.
Is there data of sufficient quality, quantity and representativeness to assess the current state of the attribute on a national scale?	It is not entirely clear whether SoE data adequately represents the maximum conditions or not.
5. Implications of including the attribute in the NOF	
Do we understand/can we estimate the extent (spatial), magnitude, and location of failures to meet the proposed bottom line for the attribute on a national scale?	This would need to be determined after completing the proposed attribute table, but it is likely that many urban streams would fall below the bottom line.
Do we understand the implications for socio-economic impacts.	This has not been assessed as it was outside the scope of this project.

6.3 Recommendations for further work

A number of recommendations have been proposed within this report and are collated below. The recommendations are here divided into two categories: 1) tasks required to develop an attribute table; and 2) tasks required to determine if current AC monitoring is sufficient to assess compliance with those attribute tables.

Tasks required to develop attribute tables:

1. Replace ANZECC (2000) guidelines in the strawman table with revised ANZECC guidelines when released (likely 2019), in line with the expanded toxicity database and the new ANZECC guidance for chronic definitions, endpoints, statistical fitting, and toxicity modifying factors.
2. Assess the best option for acute thresholds in the attribute tables given the short-comings of the US EPA criteria. If acute ANZECC guidelines are developed, these could be used for thresholds in preference to US EPA CMC values.
3. Assess whether to incorporate speciation and bioavailability of Cu and Zn, through either use of look-up tables and equations to adjust threshold values; or using a Biotic Ligand Model (BLM) or simplified BLM tool to estimate bioavailable concentrations to compare to values in the attribute table; or developing a tool that provides band thresholds based on local water chemistry.
4. Investigate the concentrations during high flows in urban streams and their importance, by:
   - Collating and analysing existing data on dissolved Cu and Zn concentrations over full storm event hydrographs, to define the first flush effect, and the length of time organisms are exposed to high concentrations.
   - Assess whether storm-related exposures are likely to cause acute toxicity, based on observed duration and in reference to New Zealand and international literature for tests of acute exposures (short-term) and pulsed exposures (repetitive short-term exposures).
5. Investigate the implications of using a maximum sample statistic compared to a 95th percentile, including whether ongoing monitoring programmes are able to accurately determine a maximum (i.e., whether sampling is biased to lesser flow conditions and/or too infrequent to resolve maxima) and the implications of the permissible exceedances if percentiles are used.
6. Assess the implications of the final attribute table for integrating freshwater with coastal management (e.g., estuarine management outcomes, including sediment quality).

Tasks required to determine if current AC monitoring is sufficient to assess compliance with those attribute tables:

1. Further analyse the flow-concentration relationships for the Auckland SoE data to determine whether sampling has occurred during peak flows and first-flush, to determine whether the dataset adequately covers maximum or acute conditions.
2. Examine the relationship between “average” (median or mean) concentrations and maximum concentrations in urban streams. Can measuring and assessing “average conditions” also predict or protect from maximum conditions?
3. Collate and analyse stream hardness, pH, DOC data for Auckland and from other locations to assess how this varies during storm events, and what values are most appropriate to use when comparing to attribute tables.

If the SoE monitoring does not adequately cover maximum or acute conditions, and an acute threshold is included in the attribute table, there will need to be consideration of whether there needs to be sampling that targets storm events to ensure that maximum conditions are measured. Storm event sampling can be challenging and resource-intensive and the need for this may make it difficult for Councils to assess compliance.

As described throughout this document, developing the final attribute table is still quite complex because:

- The ANZECC guidelines are under revision.
- ANZECC (2000) specifies a decision tree approach for further investigations, an approach which is not readily compatible with a NOF attribute. Bioavailability may need to be incorporated within the attribute tables in a different way.
- Urban streams are highly flashy and experience wide ranges in concentrations which may be difficult to deal with under the NOF framework. The ranges are much greater than those experienced for contaminants such as nitrate-N in rivers and lakes that are currently included in the NOF and probably influenced its present form.
- The attributes need to take into account at least “average” conditions (baseflow) which represent long exposures and also short exposures of high concentrations as may occur under storm runoff conditions (storm flows).
- The attribute table needs to also consider the implications for estuarine receiving waters and sediments.
- The attributes, if possible, should not require complex sampling protocols, analytical methods and management decision criteria.

7 Acknowledgements

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Data for this report were provided by Auckland Council RIMU staff (including Marcus Cameron, Laura Buckthought and Kristi Holland); Greater Wellington Regional Council and Environment Canterbury; and Morphum Environmental (Mark Lowe).

8 References

ANZECC 2000. *Australian and New Zealand guidelines for fresh and marine water quality*. October 2000 edn, National Water Quality Management Strategy Paper No. 4, Australian and New Zealand Environment and Conservation Council and Agriculture and Resource Management Council of Australia and New Zealand, Canberra, Australia.

ARC 1992. An assessment of stormwater quality and the implications for the treatment of stormwater in the Auckland Region. Report prepared by Kingett Mitchell & Associates Limited. Environmental Planning Division Technical Publication No. 5. Auckland Regional Council. April 1992.

ARC 2004a. *Framework for Assessment and Management of Urban Streams in the Auckland Region*. ARC Technical Publication 232, Auckland Regional Council, Auckland.

ARC 2007. *State of the Environment Monitoring Groundwater Quality Data Report 1998-2005*. ARC Technical Publication 352., Auckland Regional Council, Auckland.

ARC 2008. *State of the Environment Monitoring Lake Water Quality Data Report 2006-2007*. Technical Publication 343, Auckland Regional Council, Environmental Research Monitoring and Research Group.

ASL 2013. Implementing the National Policy Statement on Freshwater Management: Recommended values and objectives for the Auckland region. Andrew.Stewart Limited (ASL) report by J. Wyeth and I. Mahew for Auckland Council, Auckland.

Auckland Council 2013a, *Auckland Council Regional Plan: Air, Land and Water*. Available from: <http://www.aucklandcouncil.govt.nz/en/planspoliciesprojects/plansstrategies/districtRegionalPlans/regionalplans/auckland-council-regional-plan-air-land-and-water/Pages/home.aspx>.

Auckland Council 2013b. *Auckland's Freshwater Programme – Wai Ora Wai Māori Tāmaki Makaurau*. Auckland Council. Available from: <http://www.aucklandcouncil.govt.nz/EN/newseventsculture/OurAuckland/PublicNotices/Pages/aucklandfreshwaterprogrammeannualprogressreport.aspx>. [10 October 2014].

Auckland Council 2014b. Proposed Auckland Unitary Plan (PAUP) (notified 30th September 2013) (*http://unitaryplan.aucklandcouncil.govt.nz/pages/plan/Book.aspx)*.

Auckland Council 2014c. *State of the Environment: Freshwater*. Auckland Council. Available from: <http://stateofauckland.aucklandcouncil.govt.nz/report-type/freshwater-report-card/>.

Batley GE, van Dam RA, Warne MS, Chapman JC, Fox DR, Hickey CW, Stauber JL. 2018. Technical rationale for changes to the method for deriving Australian and New Zealand water quality guideline values for toxicants. CSIRO Land and Water Report Prepared for the Council of Australian Government's Standing Council on Environment and Water (SCEW), Sydney, Australia. p 48.

Bio-Met 2013. Bioavailability Tool. User Guide (version 2.3). Guidance document on the use of the bio-met bioavailability tool, www.bio-met.net, Version date 08/12/2013.

Bishop, C., Buckthought, L., Cameron, M.J., Carbines, M.J., Curran-Cournane, F., Hudson, M.E., Kalbus, E., Landers, T.J., Reid, A., Reid, N., Solomon, R., Vaughan, M., Waipara, N.W., Walker, J.W., Wildish, B.R., Xie, S. 2015. The Health of Auckland's Natural Environment in 2015. Auckland Council. https://www.aucklandcouncil.govt.nz/environment/state-of-auckland-research-report-cards/Documents/stateofenvironmentreport2015.pdf

Buckthought, L E and Neale, M W (2016). State of the environment monitoring: river water quality state and trends in Auckland 2005-2014. Auckland Council technical report, TR2016/008

Clearwater SJ, Thompson KA, Hickey CW. 2014. Acute toxicity of copper, zinc and ammonia to larvae (glochidia) of a native freshwater mussel *Echyridella menziesii* in New Zealand. *Archives of Environmental Toxicology and Chemistry*, 66: 213-226.

Diffuse Sources 2004. Project Twin Streams Water Quality Monitoring. Summer 2003-2004. Report prepared for EcoWater Solutions Waitākere City Council, by Diffuse Sources Ltd, in collaboration with Enviro-Ventures & Associates Ltd andd Kingett Mitchell & Associates Ltd. June 2004.

Diffuse Sources 2005. Project Twin Streams Pressure-State Analysis. An Initial Evaluation using Water & Sediment Quality Data from Summer 2003-2004. Report prepared for EcoWater Solutions Waitākere City Council, by Diffuse Sources Ltd, in collaboration with Enviro-Ventures & Associates Ltd andd Kingett Mitchell & Associates Ltd. August 2005.

Diffuse Sources 2006. Project Twin Streams Water Quality Monitoring. Summer 2005-2006. Report prepared for EcoWater Solutions Waitākere City Council, by Diffuse Sources Ltd, in collaboration with Enviro-Ventures & Associates Ltd andd Kingett Mitchell & Associates Ltd. June 2006.

Evans C, Davies TD. 1998. Causes of concentration/discharge hysteresis and its potential as a tool for analysis of episode hydrochemistry. Water Resources Research 34(1): 129-137.

Gadd J, Moores J, Pattinson P, Hyde C. 2009. Stormwater and stream water quality monitoring: Bowden Road and Meadowbank Stream. Prepared for Metrowater Limited and Auckland City Council. NIWA Client Report: AKL-2009-052. October 2009.

Gadd, J. 2016. Urban streams water quality state and trends. Prepared by NIWA for Ministry for the Environment. MfE Publication reference number CR265. Published April 2017.

Gadd J, Hickey C. 2016. Guidelines for the protection of aquatic ecosystems, toxicant trigger values: Copper – Freshwater. Australian and New Zealand guidelines for fresh and marine water quality. Draft September 2016; Council of Australian Governments Standing Council on Environment and Water: Canberra, ACT, Australia, September 2016, 2016; p 31.

Gadd J, Hickey C. 2016. Guidelines for the protection of aquatic ecosystems, toxicant trigger values: Zinc – Freshwater. Australian and New Zealand guidelines for fresh and marine water quality. Draft September 2016; Council of Australian Governments Standing Council on Environment and Water: Canberra, ACT, Australia, September 2016, 2016; p 33.

Griffiths G, Timperley M. 2005. Auckland City stormwater – A summary of NIWA and other relevant studies. Prepared by NIWA for Metrowater Ltd. NIWA Client Report AKL2005-007, October 2005.

Hickey CW. 2000. Ecotoxicology: laboratory and field approaches. *In* New Zealand stream invertebrates: Ecology and implications for management. *Eds*. Collier K, Winterbourn M. p313-343.

Hickey CW,and Golding LA. 2002. Response of macroinvertebrates to copper and zinc in a stream mesocosm. *Environmental Toxicology and Chemistry*, 21: 1854-1863.

Hickey CW, Williamson RB, Green MO, Storey RG. 2016. Technical aspects of integrating water quality science in the freshwater and coastal environments. Prepared by NIWA for Auckland Regional Council. Technical Report 2016/039.

Karr, J. R. 1999. Defining and measuring river health. Freshwater Biology, 41: 221-234. doi:10.1046/j.1365-2427.1999.00427.x

Lockie S, Neale MW. 2014. State of the environment monitoring: river water quality annual report 2013. Auckland Council technical report, TR2014/032.

Margetts, B. and W. Marshall 2015. Surface water quality monitoring report for Christchurch City waterways: January-December 2014. Christchurch City Council Report. Christchurch, New Zealand., Christchurch City Council and Aquatic Ecology Limited. 102 p.

Markich SJ, Batley GE, Stauber JL, Rogers NJ, Apte SC, Hyne RV, Bowles KC, Wilde KL, Creighton NM. 2005. Hardness corrections for copper are inappropriate for protecting sensitive freshwater biota. Chemosphere 60, 1-8.

Markich SJ, King AR, Wilson SP. 2006. Non-effect of water hardness on the accumulation and toxicity of copper in a freshwater macrophyte (*Ceratophyllum demersum*): How useful are hardness-modified copper guidelines for protecting freshwater biota? Chemosphere 65(10), 1791-1800.

MfE 2011. *National Policy Statement for Freshwater Management*. Ministry for the Environment, Wellington.

MfE 2013. Proposed amendments to the National Policy Statement for Freshwater Management 2011: A discussion document. ME 1130, Ministry for the Environment, Wellington.

MfE 2014. *National Policy Statement for Freshwater Management 2014: Draft Implementation Guide*. ME 1162, Ministry for the Environment, Wellington. (http://www.mfe.govt.nz/publications/fresh-water/national-policy-statement-freshwater-management-2014-draft-implementation).

MfE 2017. *National Policy Statement for Freshwater Management 2014 (amended 2017). (http://www.mfe.govt.nz/publications/fresh-water/national-policy-statement-freshwater-management-2014-amended-2017)*. Ministry for the Environment, Wellington.

MfE. 2018. A Guide to Attributes in Appendix 2 of the National Policy Statement for Freshwater Management (as amended 2017). Wellington: Ministry for the Environment.

Mills G, Williamson RB. 2008. *The impact of urban stormwater in Auckland's Aquatic Receiving Environment. A Review of Information 1995-2005*. Auckland Reginal Council Technical Report TR2008/023, Prepared by Diffuse Sources for Auckland Regional Council.

Moores J, Reed J, Pattinson P, McHugh M. 2006. Stream flow and quality monitoring: Meola Creek and Motions Creek. NIWA Client Report No. AKL2006-009. 38 p.

O'Sullivan A, Charters F. 2013. Haytons Stream 2013 water quality investigation at Gerald Connolly Place. Report prepared by University of Canterbury. Environment Canterbury Regional Council Report No. R14/33.

Paquin, P.R., J.W. Gorsuch, S. Apte, G.E. Batley, K.C. Bowles, P.G.C. Campbell, C.G. Delos, D.M. Di Toro, R.L. Dwyer, F. Galvez, R.W. Gensemer, G.G. Goss, C. Hogstrand, C.R. Janssen, J.C. McGeer, R.B. Naddy, R.C. Playle, R.C. Santore, U. Schneider, W.A. Stubblefield, C.M. Wood and K.B. Wu. 2002. The bitoic ligand model: A historical overview. Comparative Biochemistry and Physiology Part C 133:3-35.

Perrie, A., S. Morar, J. Milne and S. Greenfield 2012. River and stream water quality and ecology in the Wellington region: State and trends. Greater Wellington Regional Council, Publication No. GW/EMI-T-12/143. Wellington, New Zealand., Greater Wellington Regional Council. 102 p.

Reed J, Timperley M. 2004. Stream flow and stormflow water quality monitoring: Oakley Creek and Whau River. NIWA Client Report No. HAM2003- 085. 25 p.

Santore, R.C., D.M. Di Toro and P.R. Paquin, H.E. Allen, and J.S. Meyer. 2001. A Biotic Ligand Model of the Acute Toxicity of Metals. II. Application to Acute Copper Toxicity in Freshwater Fish and Daphnia. *Environmental Toxicology and Chemistry*. 20(10):2397-2402.

Scarsbrook M. 2007. River Water Quality. State and Trends in the Auckland Region. Auckland Regional Council Technical Publication TP336. September 2007.

Shamseldin, A.Y. (2011). First Flush Analysis in the Auckland Region. Prepared by Auckland UniServices Ltd for Auckland Regional Council. Auckland Council Technical Report 2011/007.

Smith KS, Balistrieri LS, Todd AS. 2015. Using biotic ligand models to predict metal toxicity in mineralized systems. Applied Geochemistry 57, 55-72.

Trowsdale S. 2005. Hydrology and hydrogeochemistry of three NZ catchments with different land use. Report by Landcare for Waitākere City Council.

US EPA 1984. *Ambient water quality criteria for lead – 1984*. EPA 440/5-84-027, United States Environmental Protection Agency, Office of Water, Washington D.C.

US EPA 1986. *Quality criteria for water 1986*. EPA 440/5-86-001, United States Environmental Protection Agency, Office of Water, Regulation and Standards Division, Washington D.C.

US EPA 1995. *1995 updates : water quality criteria documents for the protection of aquatic life in ambient water*. EPA 820-B-96-001, United States Environmental Protection Agency, Office of Water, Washington D.C.

US EPA 2007. *Aquatic life ambient freshwater quality criteria – copper. 2007 Revision*. EPA-822-R-07-001, United States Environmental Protection Agency, Criteria and Standards Division, Washington, D.C.

van Genderen E, Adams W, Cardwell R, Volosin J, Santore R, Rodriguez P. 2009. An evaluation of the bioavailability and aquatic toxicity attributed to ambient zinc concentrations in fresh surface waters from several parts of the world. *Integrated Environmental Assessment and Management*, 5: 426-434.

Warne MStJ, Batley GE, van Dam RA, Chapman JC, Fox DR, Hickey CW and Stauber JL 2018. Revised Method for Deriving Australian and New Zealand Water Quality Guideline Values for Toxicants – update of 2015 version. Prepared for the revision of the Australian and New Zealand Guidelines for Fresh and Marine Water Quality. Australian and New Zealand Governments and Australian state and territory governments, Canberra, 48 pp.

Williamson RB. 1986. Urban stormwater quality II. Comparison of three urban catchments. New Zealand Journal of Marine and Freshwater Research 20: 315-328.

Williamson RB, Mills, G, Hickey CW, Cameron M, Vigar N, Buckthought L, Milne J, Stevenson M. 2015. Development of Copper and Zinc as Auckland Specific Attributes for Ecosystem Health: Part 1 Determining procedure and gaps. Working report for discussion only. Prepared by Diffuse Sources Ltd for Auckland Council. September 2015.

Williamson RB, Hickey CW, Robertson BM. 2017. Preliminary Assessment of Limits and Guidelines Available for Classifying Coastal Waters. Report for Auckland Council by Diffuse Sources Ltd. Revised May 2015. Technical Report 2017/035.

Appendix A: Zinc and copper versus land use

Land use data were received from Mark Lowe (Morphum Environmental, 23/06/15). This included CLM, LCDB4 (summer 2012/13), and PAUP data sets for the catchments upstream of the 24 water quality sites where metals have been measured.

Land use categories used to estimate “urban” land use were anything that would “generate” (or efficiently transport) contaminants.

- CLM: paved surface (commercial, industrial, residential), roofs (commercial, residential, industrial – these are given for four time periods – pre-1995, 1995-2006, after 2006, and unknown), roads (five vpd categories).
- LCDB: built up settlement and transport infrastructure.

Urban grassland or parkland were not included.

The above categories for each site/catchment were aggregated as “area” (actual area) and as “% urban area” (% of catchment area). Data are summarised in the Table below.

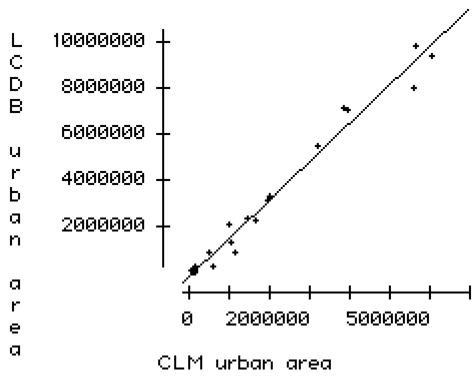
	CLM			LCDB4		
Site	catchment	urban	urban %	catchment	urban	urban %
Avondale Stream	3387092	997011	29.44	3386132	2094232	61.85
Kumeu River	45903369	1189108	2.59	45726584	797808	1.74
Lucas Creek	6126959	1961782	32.02	6123016	3138494	51.26
Mahurangi River (Forestry HQ)	7833617	69682	0.89	7832488	0	0.00
Mahurangi River (Water Supply)	48282661	1093772	2.27	48144464	1221248	2.54
Makarau River	48305257	117195	0.24	48302076	0	0.00
Matakana River	14974860	39986	0.27	14499616	26661	0.18
Nukumea Stream	1037329	26222	2.53	1037232	16273	1.57
Oakley Creek	12276676	5676503	46.24	12271240	9846697	80.24
Okura Creek	5540765	54033	0.98	5540496	93498	1.69
Omaru Creek	4802137	2012178	41.90	4797084	3308509	68.97
Otaki Creek	914077	455137	49.79	918708	864889	94.14
Otara Creek (East Tamaki)	8743485	3865593	44.21	8736784	7204424	82.46
Otara Creek (Kennell Hill)	18330399	3206217	17.49	18321164	5500081	30.02
Oteha Stream	12207344	5621833	46.05	12211576	8086034	66.22
Pakuranga Creek (Botany Rd)	7772151	3986101	51.29	7769452	7050952	90.75
Pakuranga Creek (Greenmount Drive)	2914368	1482971	50.88	2912464	2408993	82.71
Papakura Stream	47585807	1669964	3.51	47474008	2267434	4.78
Papakura Stream (Alfriston Rd)	23272338	118166	0.51	23270328	67607	0.29
Puhinui Stream	15170025	6061147	39.95	15167328	9391582	61.92
Riverhead Forest Stream	4139071	24915	0.60	4138920	10402	0.25
Vaughan Stream	2367054	143758	6.07	2363420	189916	8.04
Wairoa River	131389234	568740	0.43	132422872	189815	0.14
Waiwera River	31775296	126939	0.40	31102432	0	0.00

A1: Comparison of CLM and LCDB values

CLM and LCDB catchment areas were very similar but “urban” areas very different.

Site	Predominant land use	LCDB/CLM ratios		
		catchment area	urban area	% urban area
Avondale Stream	urban	1.00	2.10	2.10
Kumeu River	rural	1.00	0.67	0.67
Lucas Creek	urban	1.00	1.60	1.60
Mahurangi River (Forestry HQ)	exotic forest	1.00	0.00	0.00
Mahurangi River (Water Supply)	rural	1.00	1.12	1.12
Makarau River	rural	1.00	0.00	0.00
Matakana River	rural	0.97	0.67	0.69
Nukumea Stream	native forest	1.00	0.62	0.62
Oakley Creek	urban	1.00	1.73	1.74
Okura Creek	rural	1.00	1.73	1.73
Omaru Creek	urban	1.00	1.64	1.65
Otaki Creek	urban	1.01	1.90	1.89
Otara Creek (East Tamaki)	urban	1.00	1.86	1.87
Otara Creek (Kennell Hill)	urban	1.00	1.72	1.72
Oteha Stream	urban	1.00	1.44	1.44
Pakuranga Creek (Botany Rd)	urban	1.00	1.77	1.77
Pakuranga Creek (Greenmount Drive)	urban	1.00	1.62	1.63
Papakura Stream	rural	1.00	1.36	1.36
Papakura Stream (Alfriston Rd)	rural	1.00	0.57	0.57
Puhinui Stream	urban	1.00	1.55	1.55
Riverhead Forest Stream	exotic forest	1.00	0.42	0.42
Vaughan Stream	rural	1.00	1.32	1.32
Wairoa River	rural	1.01	0.33	0.33
Waiwera River	rural	0.98	0.00	0.00

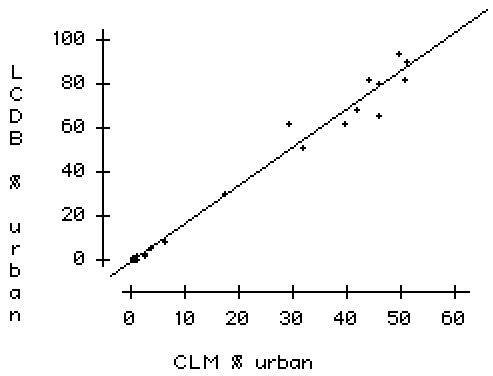
Actual ratios vary considerably for each catchment/site, but overall there is a highly significant linear relationship between the CLM and LCDB urban land use areas, on average the LCDB gave areas 1.65 times the CLM values (or 1.73 times for % urban area) – see Datadesk output below.



Dependent variable is: **LCDB urban area**
No Selector
R squared = 97.9% R squared (adjusted) = 97.8%
s = 494.9e3 with 24 - 2 = 22 degrees of freedom

Source	Sum of Squares	df	Mean Square	F-ratio
Regression	246.643e12	1	246.643e12	1.01e3
Residual	5.38784e12	22	244.902e9	

Variable	Coefficient	s.e. of Coeff	t-ratio	prob
Constant	-137959	134e3	-1.03	0.3145
CLM urban ...	1.65364	0.05211	31.7	≤ 0.0001



Dependent variable is: **LCDB % urban**
No Selector
R squared = 98.3% R squared (adjusted) = 98.3%
s = 4.871 with 24 - 2 = 22 degrees of freedom

Source	Sum of Squares	df	Mean Square	F-ratio
Regression	30967.4	1	30967.4	1.3e3
Residual	522.079	22	23.7309	

Variable	Coefficient	s.e. of Coeff	t-ratio	prob
Constant	-0.996484	1.369	-0.728	0.4743
CLM % urban	1.73345	0.04799	36.1	≤ 0.0001

A2: Comparison with “estimated areas” and state of the environment 2007 report values

Data used in the initial box plots of metals concentrations versus site, with approximately increasing per cent urban area, was a mixture of per cent urban area data given in the ARC 2007 SoE report (18 sites) and for six sites, estimates made from visual inspection of topo maps and aerial photos (AC GIS viewer).

The per cent urban area data from the initial “estimates/SoE values” are compared with the CLM and LCDB values in the table and Datadesk outputs below.

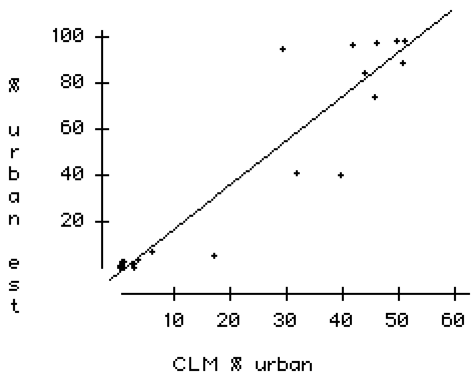
The “estimates/SoE values” were, on average, considerably (1.92 times) lower than the CLM values, and showed considerable variation for individual sites. Otara (Kennel Hill), Puhinui, and Lucas Creek had per cent urban areas markedly lower than the “average” “estimated/SoE area”: CLM area, while Avondale was markedly higher.

The “estimates/SoE values” were, on average, similar to (1.12 times higher) the LCDB values, and showed less variation for individual sites than for the CLM data. Otara (Kennel Hill), Puhinui, and Lucas Creek again had per cent urban areas markedly lower than the “average” “estimated/SoE area”: CLM area, while Avondale and Omaru were somewhat higher. The 2007 SoE report land use values from the LCDB used LCDB2, an earlier version, based on satellite data from 2001/02. There has been urban development in the catchment of some streams between 2001/02 and 2012/13.

Site	% urban est	CLM % urban	LCDB % urban
Makarau River	0.1	0.24	0.00
Matakana River	0	0.27	0.18
Waiwera River	0	0.40	0.00
Wairoa River	0	0.43	0.14
Papakura Stream (Alfriston Rd)	2	0.51	0.29
Riverhead Forest Stream	0	0.60	0.25
Mahurangi River (Forestry HQ)	0	0.89	0.00
Okura Creek	2	0.98	1.69
Mahurangi River (Water Supply)	1.7	2.27	2.54
Nukumea Stream	0	2.53	1.57
Kumeu River	0.9	2.59	1.74
Papakura Stream	2.9	3.51	4.78
Vaughan Stream	6.7	6.07	8.04
Otara Creek (Kennell Hill)	4.8	17.49	30.02
Avondale Stream	95	29.44	61.85
Lucas Creek	41.4	32.02	51.26
Puhinui Stream	40.5	39.95	61.92
Omaru Creek	97	41.90	68.97
Otara Creek (East Tamaki)	84.9	44.21	82.46
Oteha Stream	74.3	46.05	66.22
Oakley Creek	97.7	46.24	80.24
Otaki Creek	98.5	49.79	94.14
Pakuranga Creek (Greenmount Drive)	89.5	50.88	82.71
Pakuranga Creek (Botany Rd)	99.1	51.29	90.75

% urban data from 2007 SoE report used in prelim plots

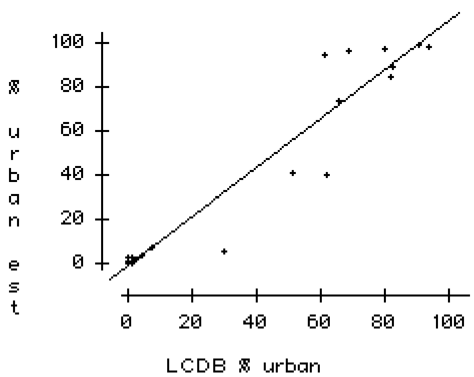
% urban estimated from topo maps/aerials used in prelim plots & analyses



Dependent variable is: **% urban est**
No Selector
R squared = 89.2% R squared (adjusted) = 88.7%
s = 14.41 with 24 - 2 = 22 degrees of freedom

Source	Sum of Squares	df	Mean Square	F-ratio
Regression	37782	1	37782	182
Residual	4571.33	22	207.788	

Variable	Coefficient	s.e. of Coeff	t-ratio	prob
Constant	-2.58181	4.051	-0.637	0.5305
CLM % urban	1.9147	0.142	13.5	≤ 0.0001



Dependent variable is: **% urban est**
No Selector
R squared = 92.7% R squared (adjusted) = 92.4%
s = 11.83 with 24 - 2 = 22 degrees of freedom

Source	Sum of Squares	df	Mean Square	F-ratio
Regression	39276	1	39276	281
Residual	3077.29	22	139.877	

Variable	Coefficient	s.e. of Coeff	t-ratio	prob
Constant	-1.88535	3.265	-0.577	0.5695
LCDB % urb...	1.11681	0.06665	16.8	≤ 0.0001

Appendix B: Total/soluble relationships

We investigated total:soluble metals relationships to assess whether the two forms are well enough correlated to predict one from the other.

The relationship was investigated in two ways:

- Linear regressions of total vs soluble metals – slope and significance. Visual assessment of scatter plots was used as a check of data integrity (major outliers, (non)linearity).
- Total:soluble metals ratios calculated from each sample. Statistical summaries of medians (and means) and spread were prepared.

These assessments were carried out for individual sites, by major land use groups (native forest, exotic forest, rural, and urban) and for all sites grouped.

B1: Total/soluble metals relationships from linear regression analysis

Scatter plots of total versus soluble metals concentrations were also generated to assist in visual assessment of the relationships (e.g. identify outlying data or unusual results). Plots for all sites grouped are shown in Figure B-1, and by land use class in Figure B-2 (Cu) and Figure B-3 (Zn). Plots for individual sites have not been presented here.

Linear regression analysis of total versus soluble Cu and Zn was undertaken for each site, for sites grouped into each land use class, and for all sites grouped. The results were expressed in terms of the slope of the regression, the "goodness of fit" (R^2, or coefficient of determination), and the statistical significance (p value). The results of the regressions are summarised in Table B-1. Summaries of the linear regression slopes are also presented in bar charts (Figure 0-4), box plots for all sites (Figure B-5) and for sites grouped by land use (Figure B0-6). These plots show the variability in regression slopes and permit assessment of the differences between sites and land use classes.

Generally there is a significant linear relationship between the total and soluble forms of Cu and Zn. For all site data grouped, Total Zn = 1.67 x soluble Zn. Total Cu = 1.35 x soluble Cu. The median of all sites has Total Zn = 1.23 x soluble Zn. Total Cu = 1.44 x soluble Cu.

The relationships between total and soluble metals varied considerably between sites and land use groupings. For Zn, the range in regression slopes was 0.63-3.39 and for Cu the range was 0.62-3.01. The values <1 indicate problems with the data, as total concentrations can't be less than the soluble. Outlying data has the potential to influence the regressions; e.g. for Oakley Creek, removal of one very high outlying soluble Zn result changed the slope from 0.719 to 1.332. Regressions having high intercepts may also be responsible for some of the "<1" slopes.

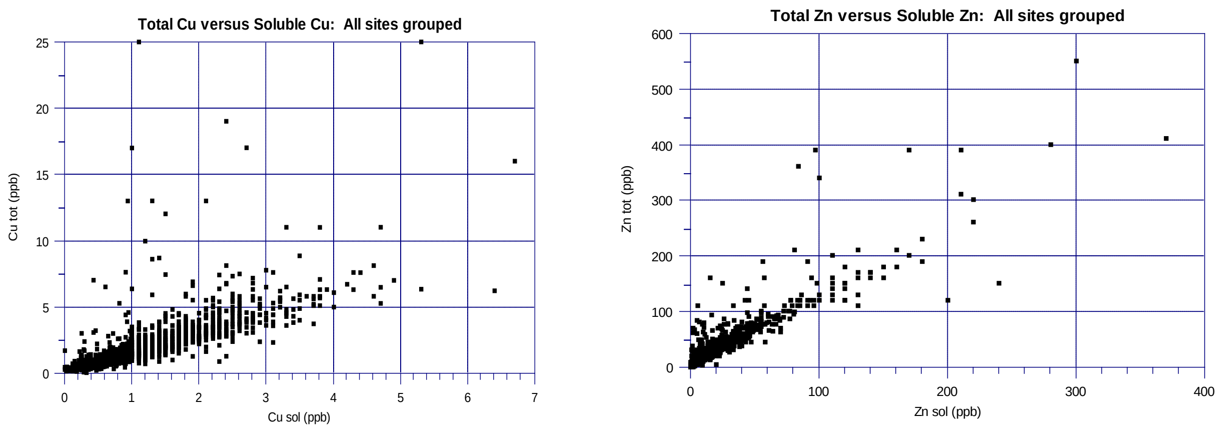


Figure B-1 Scatter plots of total versus soluble Cu and Zn. Data are from all sites grouped.

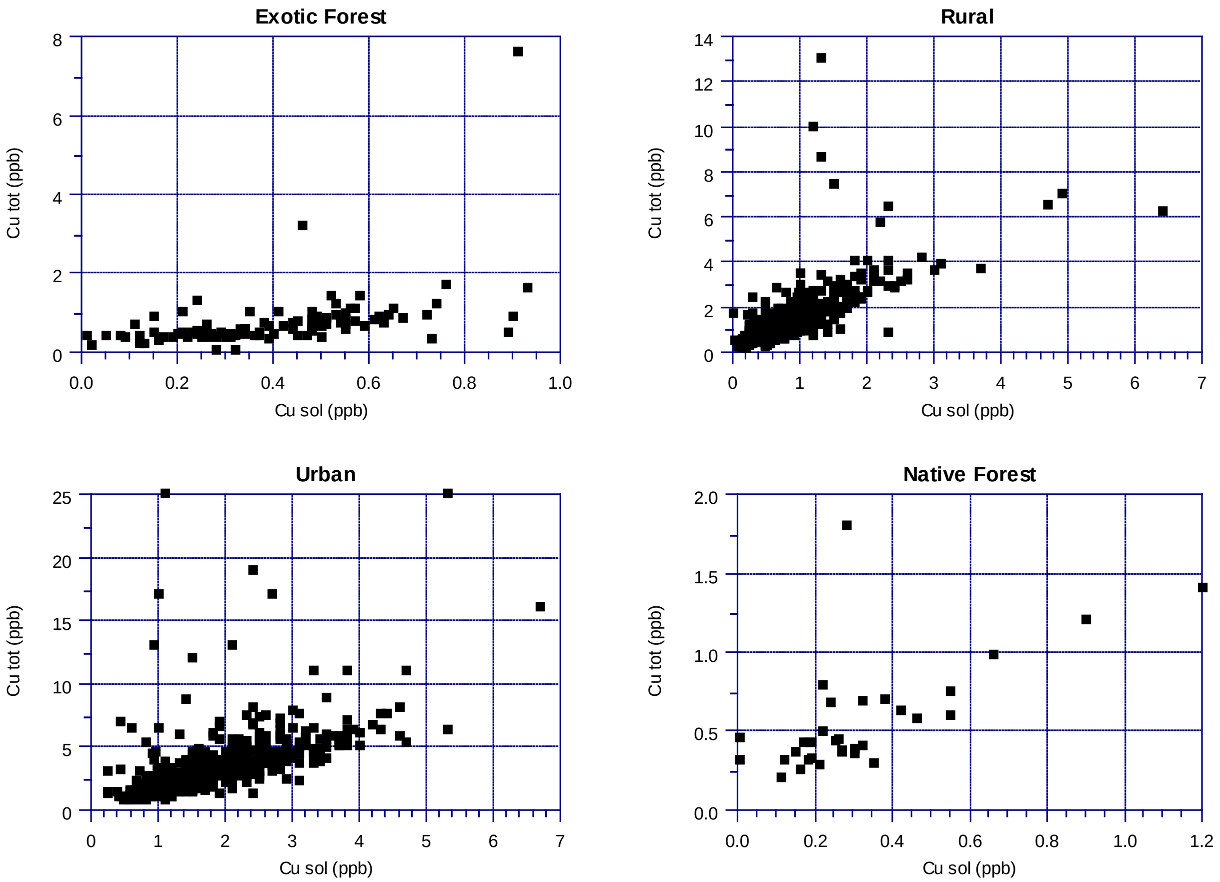


Figure B-2 Scatter plots of total versus soluble copper. Data are grouped by land use.

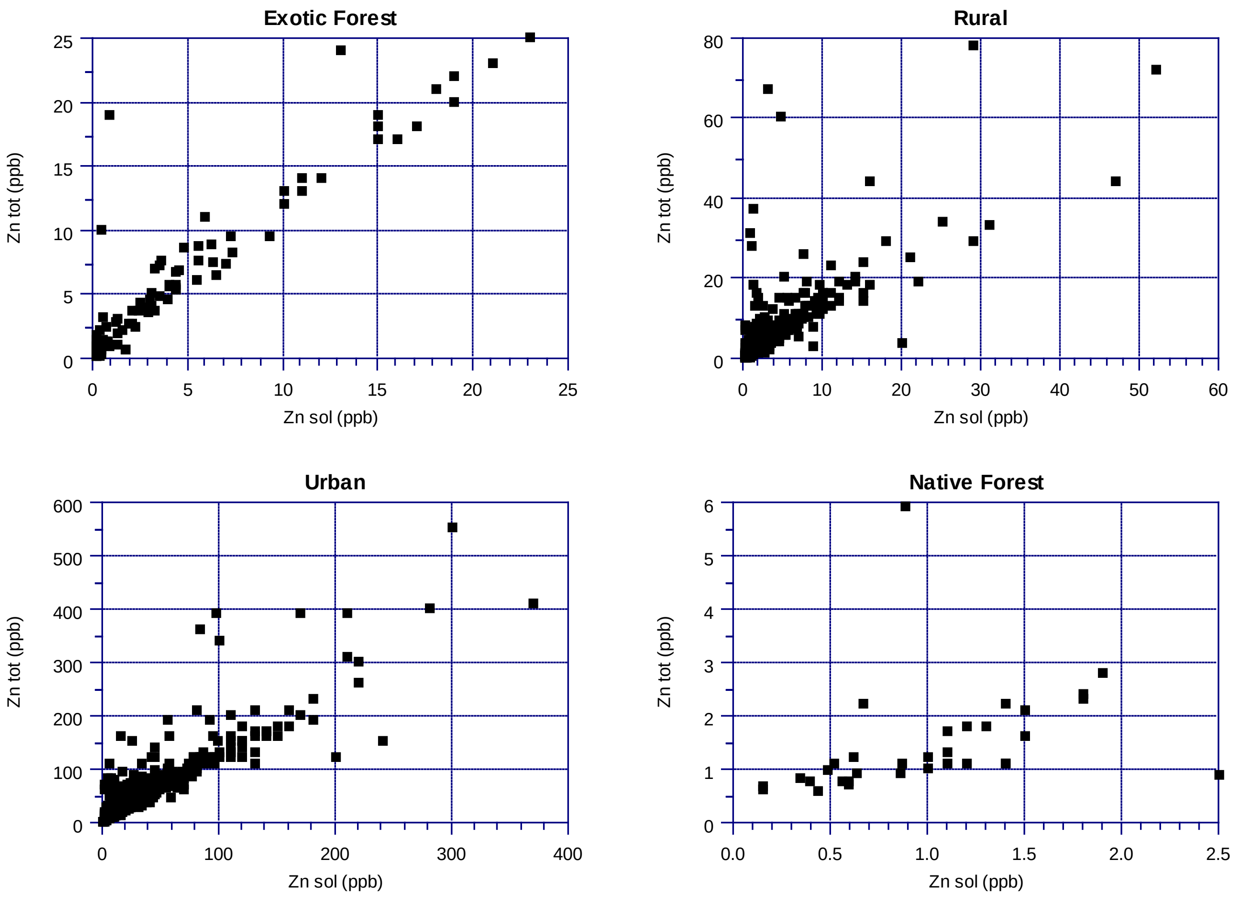


Figure B-3 Scatter plots of total versus soluble zinc. Data are grouped by land use.

Even though there are lots of data (high “N”), outliers appear to affect the robustness of the regression slope analysis. Improved estimates might be obtained by looking at all “outlying” data points at each site. Flow may also be a contributing factor to the outlying results – it may be that at high (or very low) flows the “typical” linear relationship that exits under most conditions doesn’t apply.

Riverhead Stream was a site notable for its almost perfect total:soluble Zn linear relationship, with essentially all Zn in soluble form. Along with the relatively elevated Zn concentrations at this exotic forest site, the regression analysis suggests the Zn source at Riverhead is atypical.

Table B-1 Linear regression results for total versus soluble metals for a) data from all sites grouped, b) data grouped by land use, and c) individual streams. Highlighted values are linear regression slopes clearly less than 1 (indicating soluble > total metals, which is not possible and therefore requires further investigation to understand).

	Total: Soluble Copper				Total: Soluble Zinc			
Site or Land Use	slope	R^2	p	N	slope	R^2	p	N
All sites grouped	1.671	0.518	0.000	1732	1.347	0.830	0.000	1734
Exotic forest	1.828	0.201	0.000	102	1.097	0.868	0.000	102
Native forest	0.951	0.409	0.000	33	0.620	0.087	0.053	33
Rural	1.317	0.495	0.000	609	1.267	0.564	0.000	609
Urban	1.692	0.418	0.000	988	1.307	0.802	0.000	990
Mahurangi FHQ	3.390	0.330	0.000	51	1.768	0.569	0.000	51
Riverhead	0.694	0.296	0.000	51	1.046	0.967	0.000	51
Nukumea	0.951	0.409	0.000	33	0.620	0.087	0.053	33
Matakana	2.383	0.455	0.000	50	1.148	0.503	0.000	50
Wairoa	0.634	0.166	0.002	51	0.919	0.929	0.000	51
Waiwera	2.083	0.214	0.000	51	0.822	0.245	0.000	51
Makarau	2.702	0.267	0.000	51	3.007	0.120	0.007	51
Kumeu	1.287	0.688	0.000	51	1.178	0.808	0.000	51
Mahurangi WS	2.297	0.433	0.000	51	1.485	0.185	0.001	51
Okura	1.412	0.801	0.000	111	1.560	0.479	0.000	111
Papakura AR	1.036	0.925	0.000	32	1.416	0.852	0.000	32
Papakura PR	1.345	0.811	0.000	51	1.317	0.754	0.000	51
Otara KH	1.866	0.349	0.000	110	1.675	0.820	0.000	110
Vaughan	1.042	0.776	0.000	110	1.252	0.645	0.000	110
Puhinui	1.598	0.355	0.000	110	1.200	0.729	0.000	111
Lucas	1.627	0.769	0.000	111	2.819	0.409	0.000	111
Oteha	1.438	0.605	0.000	111	1.141	0.558	0.000	111
Otara ET	2.810	0.472	0.000	84	1.660	0.603	0.000	84
Pakuranga GD	1.965	0.769	0.000	83	1.371	0.934	0.000	84
Avondale	1.421	0.682	0.000	33	1.154	0.806	0.000	33
Omaru	1.725	0.361	0.000	68	1.262	0.714	0.000	68
Oakley	1.407	0.432	0.000	110	0.719	0.595	0.000	110
Otaki	1.434	0.475	0.000	84	1.024	0.825	0.000	84
Pakuranga BR	1.381	0.101	0.002	84	1.173	0.713	0.000	84
mean	1.664				1.364			
median	1.436				1.226			
minimum	0.634				0.620			
maximum	3.390				3.007			
5%ile	0.733				0.734			
95%ile	2.794				2.661			

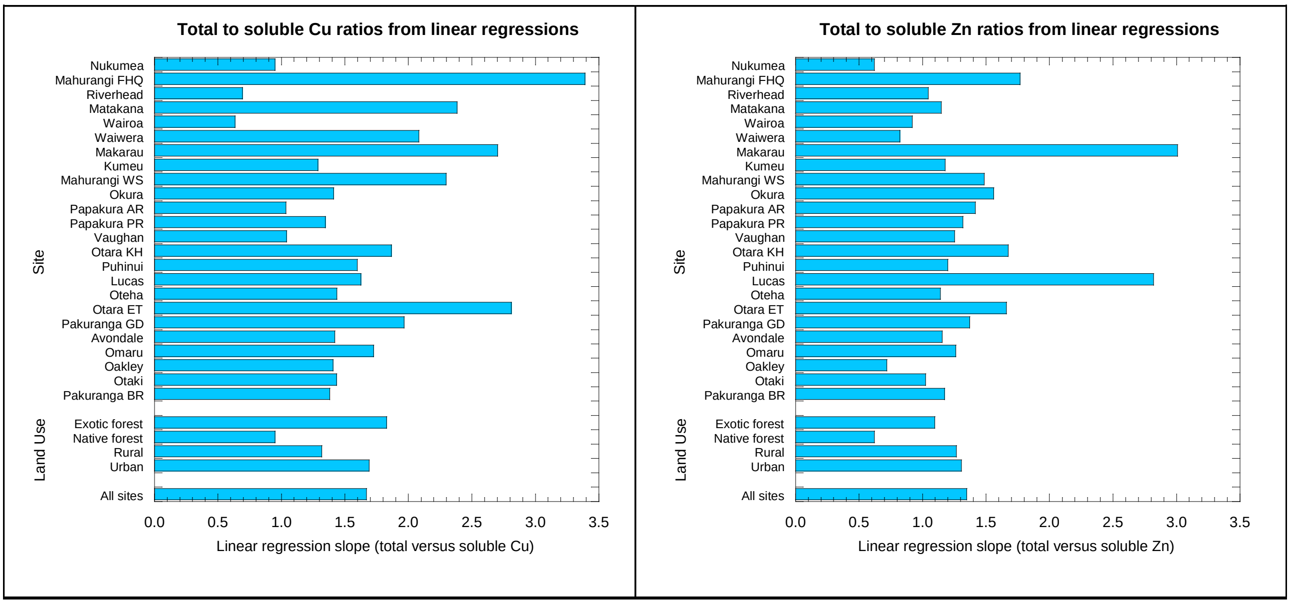


Figure 0-4 Linear regression slopes for total versus soluble metals at individual sites, for each land use class, and for all sites grouped.

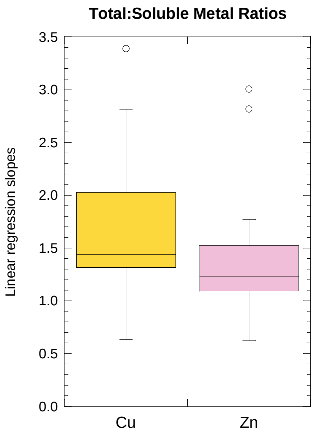


Figure B-5 Box plot of linear regression slopes from total versus soluble metals. Data are for all sites grouped. The plot shows the medians and range of linear regression slopes of the total versus soluble metal plots.

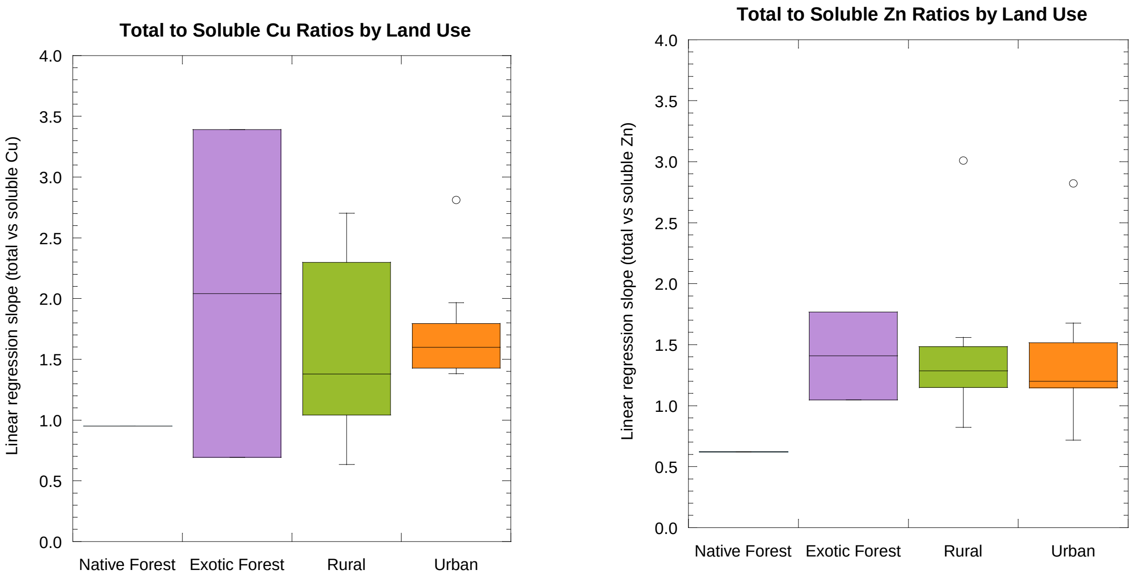


Figure B0-6 Box plots of total: soluble metal ratios obtained from linear regression slopes. The data plotted are median slopes from each site within each land use group. The figure shows reasonably consistent overall median "ratios" between total and soluble zinc (Zn) across the land use groups, while Cu showed more variability, particularly for exotic forest (where there were only two sites).

B2: Total/soluble metals ratios calculated from each sample

The total/soluble metal concentration ratio for each individual sample was calculated and the results summarised in variety of ways (for individual samples at each site, by land use, medians at each site etc).

Total:soluble metal ratios for individual samples were highly variable (Table B-2) and therefore application of a "conversion factor" based on a single sample ratio value may be subject to considerable uncertainty. Using median (or mean) ratios is likely to be more robust, but again use of an "averaged" ratio may not give a reliable result for individual samples.

Table B-2 Statistical summaries of total/soluble metal ratios calculated from individual samples: a) for all sites grouped, b) data grouped by land use, and c) for individual sites

A. All sites grouped

All sites grouped							
Total/Soluble ratio	Count	Mean	Median	Min	Max	5%ile	95%ile
Zinc	1734	2.24	1.60	0.19	53.33	1.00	4.70
Copper	1732	2.12	1.56	0.16	340.00	1.06	3.15

B. Data grouped by land use

By land use: Total/Soluble Copper							
Land Use	Count	Mean	Median	Min	Max	5%ile	95%ile
Native Forest	33	6.39	1.69	0.83	90.00	1.10	53.66
Exotic Forest	102	2.42	1.60	0.16	41.00	0.79	6.49
Rural	609	2.29	1.49	0.37	340.00	0.92	3.36
Urban	988	1.84	1.61	0.54	22.73	1.15	2.87

By land use: Total/Soluble Zinc							
Land Use	Count	Mean	Median	Min	Max	5%ile	95%ile
Native Forest	33	1.75	1.38	0.35	6.70	0.79	4.41
Exotic Forest	102	2.60	1.45	0.35	24.39	0.91	6.59
Rural	609	2.62	1.66	0.19	53.33	0.92	5.38
Urban	990	1.99	1.58	0.60	36.84	1.15	3.75

C. Ratios for individual sites

By site: Total/Soluble Copper								
Site	Land Use	Count	Mean	Median	Min	Max	5%ile	95%ile
Mahurangi River FHQ	Exotic forest	51	2.25	1.69	0.18	8.35	0.92	6.92
Riverhead Stream	Exotic forest	51	2.59	1.42	0.16	41.00	0.54	5.96
Nukumea @ Upper	Native forest	33	6.39	1.69	0.83	90.00	1.10	53.66
Kumeu River	Rural	51	8.12	1.41	0.92	340.00	1.09	2.28
Mahurangi River WS	Rural	51	1.91	1.51	0.77	6.62	0.87	4.51
Makarau @ Railway	Rural	51	1.80	1.45	0.67	8.33	0.94	3.98
Matakana River	Rural	50	1.71	1.50	0.59	5.86	0.85	2.71
Okura Creek	Rural	111	1.78	1.61	0.47	4.80	1.12	3.02
Papakura @ Alfriston	Rural	32	1.65	1.54	1.15	3.38	1.17	2.83
Papakura Stream	Rural	51	1.39	1.29	0.72	3.40	0.97	2.27
Vaughn Stream	Rural	110	1.91	1.49	0.61	16.00	0.90	3.50
Wairoa River	Rural	51	1.59	1.48	0.37	4.58	0.65	2.81
Waiwera Stream	Rural	51	1.84	1.50	0.67	10.00	0.86	3.95
Avondale Stream @ Sh	Urban	33	1.68	1.60	1.08	3.22	1.14	2.88
Lucas Creek	Urban	111	1.60	1.52	0.66	2.88	1.09	2.33
Oakley Creek	Urban	110	1.84	1.59	1.08	13.83	1.20	2.83
Omaru @ Maybury	Urban	68	1.94	1.66	1.00	7.92	1.29	3.12
Otaki Creek	Urban	84	2.27	1.85	0.74	16.28	1.30	4.30
Otara Ck East Tamaki	Urban	84	1.86	1.55	0.90	17.00	1.09	2.93
Otara Ck Kennel Hill	Urban	110	1.84	1.60	0.83	10.83	1.10	2.87
Oteha Stream	Urban	111	1.66	1.56	0.68	6.54	1.00	2.36
Pakuranga Ck Botany	Urban	84	2.14	1.64	1.23	22.73	1.33	3.07
Pakuranga Ck Greenmt	Urban	83	1.90	1.60	1.17	12.00	1.29	3.19
Puhinui Stream	Urban	110	1.65	1.54	0.54	6.19	1.17	2.30

By site: Total/Soluble Zinc								
Site	Land Use	Count	Mean	Median	Min	Max	5%ile	95%ile
Mahurangi River FHQ	Exotic forest	51	3.87	2.68	0.35	24.39	0.48	11.87
Riverhead Stream	Exotic forest	51	1.34	1.27	1.00	2.16	1.04	1.86
Nukumea @ Upper	Native forest	33	1.75	1.38	0.35	6.70	0.79	4.41
Kumeu River	Rural	51	2.60	1.58	0.88	53.33	1.07	2.78
Mahurangi River WS	Rural	51	2.69	1.66	1.00	28.46	1.06	7.31
Makarau @ Railway	Rural	51	4.22	2.18	0.47	52.00	0.92	20.00
Matakana River	Rural	50	2.33	1.83	0.19	15.00	0.58	4.86
Okura Creek	Rural	111	2.86	2.30	0.19	22.33	1.12	6.33
Papakura @ Alfriston	Rural	32	1.62	1.52	1.08	2.82	1.10	2.72
Papakura Stream	Rural	51	1.55	1.37	0.85	7.89	1.03	2.13
Vaughn Stream	Rural	110	2.48	1.53	0.31	45.33	0.90	4.84
Wairoa River	Rural	51	2.27	1.68	0.50	8.67	0.74	5.24
Waiwera Stream	Rural	51	3.05	1.90	0.68	36.47	0.87	5.61
Avondale Stream @ Sh	Urban	33	1.53	1.46	1.07	2.45	1.10	2.29
Lucas Creek	Urban	111	2.33	1.80	0.71	20.00	1.14	5.32
Oakley Creek	Urban	110	1.76	1.51	0.63	7.10	1.11	3.40
Omaru @ Maybury	Urban	68	1.67	1.43	1.00	8.56	1.14	3.25
Otaki Creek	Urban	84	1.85	1.55	0.85	10.83	1.17	4.01
Otara Ck East Tamaki	Urban	84	1.57	1.41	1.08	4.29	1.15	2.48
Otara Ck Kennel Hill	Urban	110	2.11	1.77	0.76	17.29	1.20	3.50
Oteha Stream	Urban	111	1.96	1.44	0.87	33.89	1.13	2.72
Pakuranga Ck Botany	Urban	84	2.68	1.87	1.00	36.84	1.20	5.62
Pakuranga Ck Greenmt	Urban	84	2.05	1.83	1.11	10.00	1.37	3.13
Puhinui Stream	Urban	111	1.94	1.55	0.60	8.17	1.09	3.81

A summary of median ratios calculated from the total/soluble metal concentrations from each individual sample are given in

Table B-3. Graphical summaries of these results are provided in Figure B-7 (bar plots showing median ratios at all individual sites, Figure B-8 (box plots for all sites grouped, showing data spread and comparison of Cu and Zn), and Figure B-9 (box plots comparing data grouped by land use).

For all site data grouped, using the median total:soluble metal ratios: Total Zn = 1.60 x soluble Zn. Total Cu = 1.56 x soluble Cu. Median ratios were reasonably consistent between sites for Cu, ranging from 1.29 to 1.85. Median ratios were more variable between sites for Zn, ranging from 1.27 to 2.68. No median ratios were <1; minimum vales for the site median ratios were 1.29 for Cu, and 1.27 for Zn. However, minimum ratios for individual samples were often <1 (see Table B-2) – as discussed for linear regression analysis, the reasons for this require further exploration.

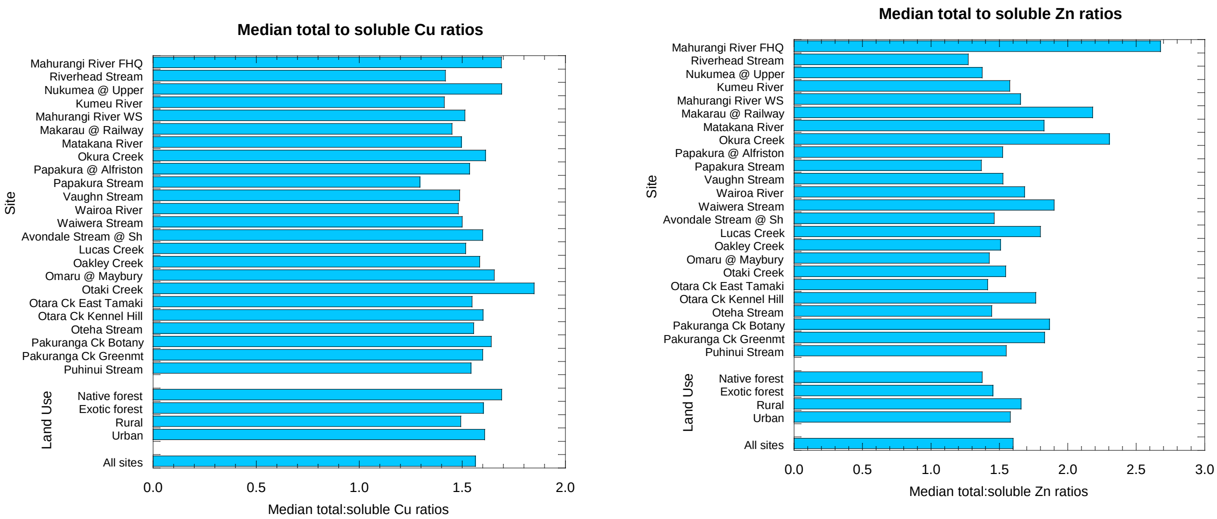


Figure B-7 Median total:soluble metal ratios at individual sites, for each land use class, and for all sites grouped.

Table B-3 A summary of median total/soluble metals concentrations for a) data from all sites grouped, b) data grouped by land use and c) individual streams.

Site/Land Use Group	Land Use	Median Total:Soluble Ratio	
		Cu	Zn
All sites		1.56	1.60
Native Forest		1.69	1.38
Exotic Forest		1.60	1.45
Rural		1.49	1.66
Urban		1.61	1.58
Mahurangi River FHQ	Exotic forest	1.69	2.68
Riverhead Stream	Exotic forest	1.42	1.27
Nukumea @ Upper	Native forest	1.69	1.38
Kumeu River	Rural	1.41	1.58
Mahurangi River WS	Rural	1.51	1.66
Makarau @ Railway	Rural	1.45	2.18
Matakana River	Rural	1.50	1.83
Okura Creek	Rural	1.61	2.30
Papakura @ Alfriston	Rural	1.54	1.52
Papakura Stream	Rural	1.29	1.37
Vaughn Stream	Rural	1.49	1.53
Wairoa River	Rural	1.48	1.68
Waiwera Stream	Rural	1.50	1.90
Avondale Stream @ Sh	Urban	1.60	1.46
Lucas Creek	Urban	1.52	1.80
Oakley Creek	Urban	1.59	1.51
Omaru @ Maybury	Urban	1.66	1.43
Otaki Creek	Urban	1.85	1.55
Otara Ck East Tamaki	Urban	1.55	1.41
Otara Ck Kennel Hill	Urban	1.60	1.77
Oteha Stream	Urban	1.56	1.44
Pakuranga Ck Botany	Urban	1.64	1.87
Pakuranga Ck Greenmt	Urban	1.60	1.83
Puhinui Stream	Urban	1.54	1.55
mean		1.55	1.69
median		1.54	1.56
minimum		1.29	1.27
maximum		1.85	2.68
5%ile		1.41	1.37
95%ile		1.69	2.29

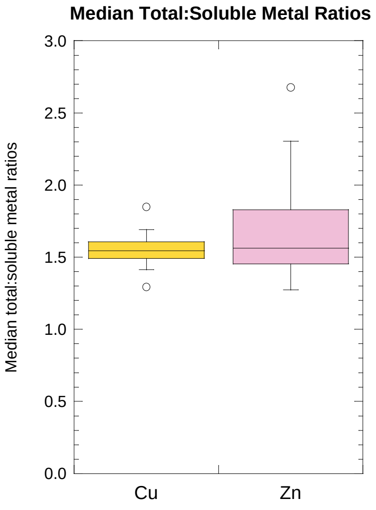
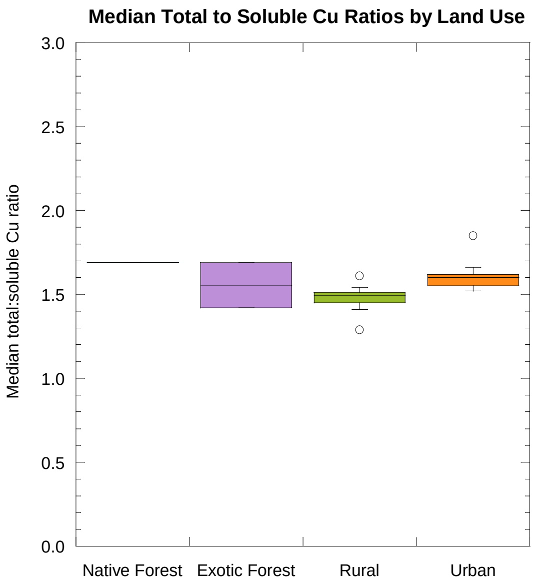


Figure B-8 Box plots of site median total: soluble metal ratios from all sites grouped.



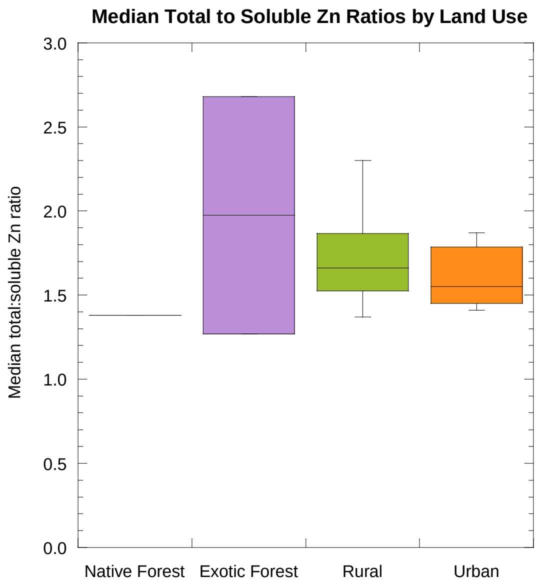
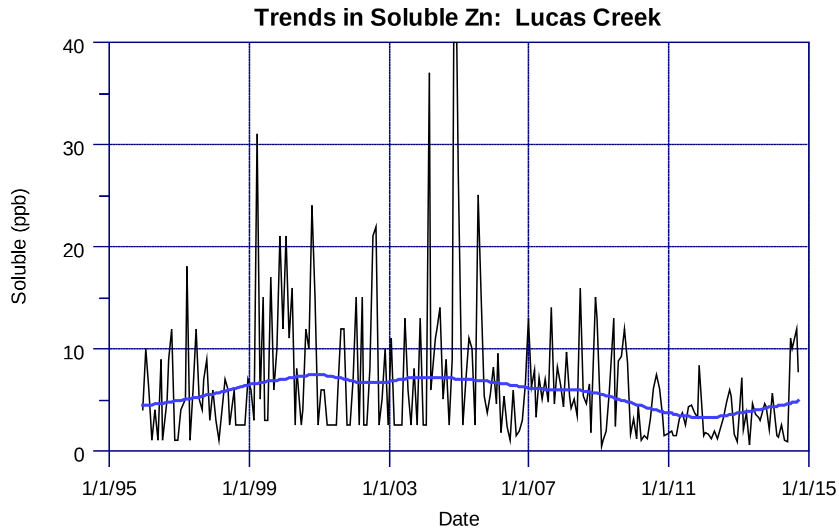


Figure B-9 Box plots of site median total: soluble metal ratios obtained from individual samples. The data plotted are median ratios from each site within each land use group. The figure shows consistent overall median ratios between total and soluble copper (Cu) across the land use groups, while Zn showed more variability, particularly for exotic forest (where there were only two sites, each of which had markedly different ratios).

Appendix C: Trend plots

Figure C-1 Soluble Zn: Lucas and Oakley Creeks



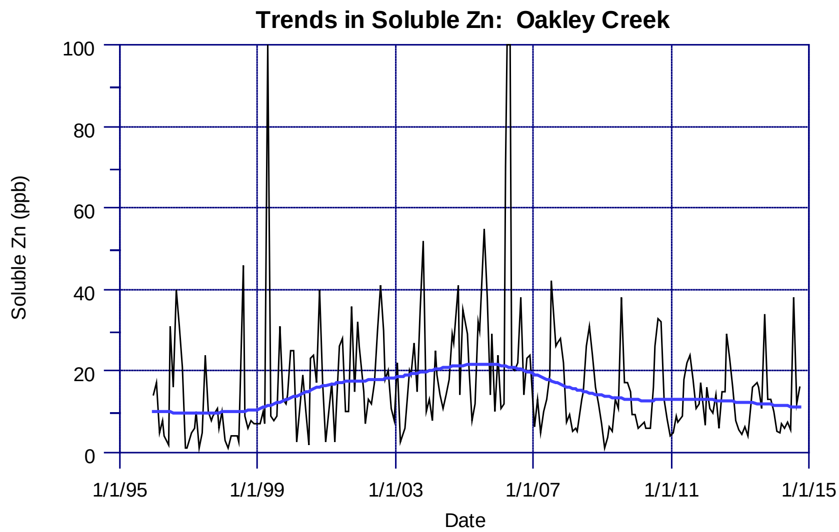
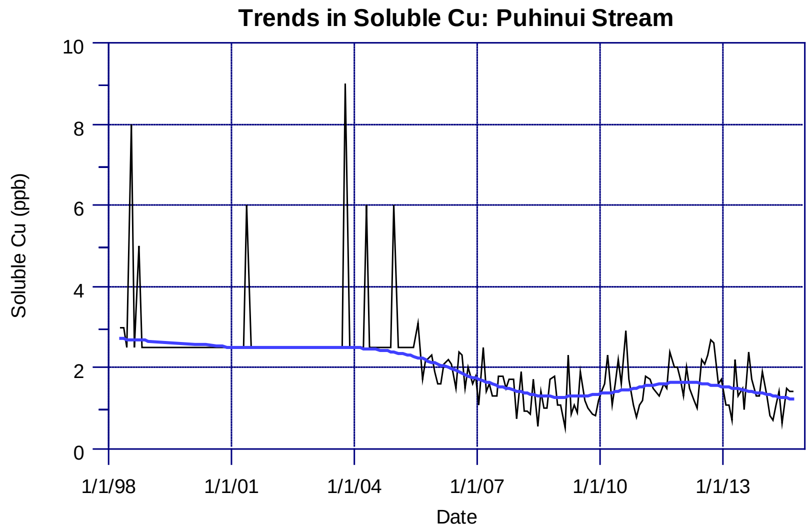
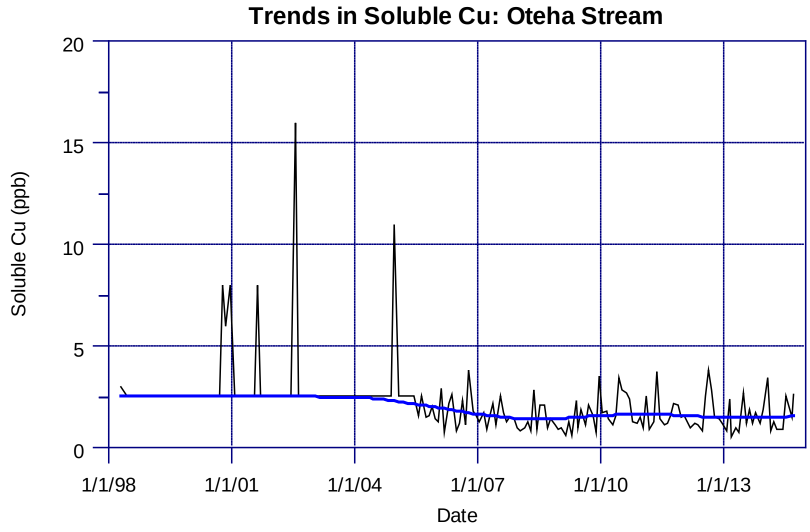
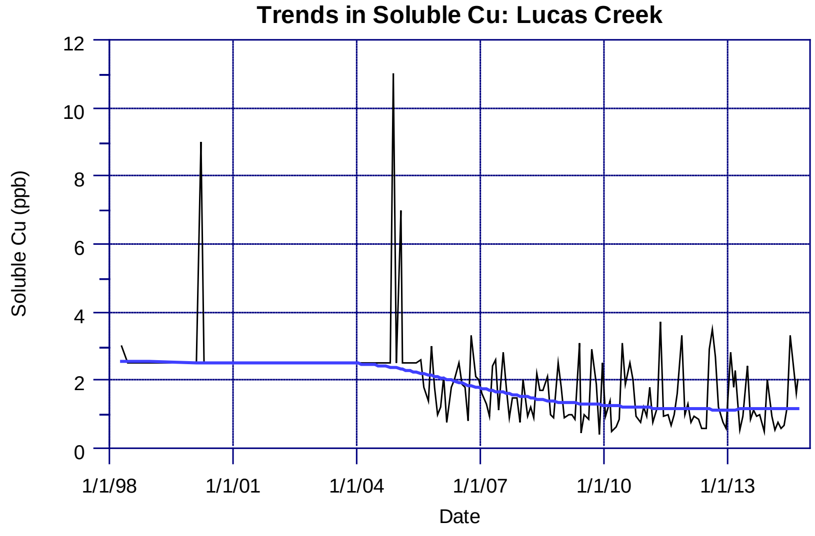
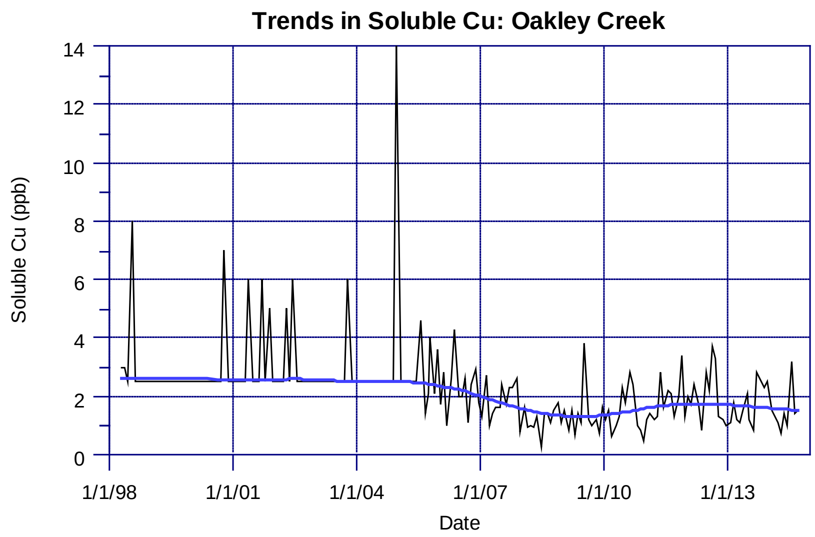


Figure C-2 Soluble Cu: Puhinui, Oteha, Lucas, and Oakley Creeks









Trends in Soluble Cu: Oakley Creek
Soluble Cu (ppb)
14
12
10
8
6
4
2
0
1/1/98
1/1/01
1/1/04
1/1/07
1/1/10
1/1/13
Date

Appendix D: Seasonality plots

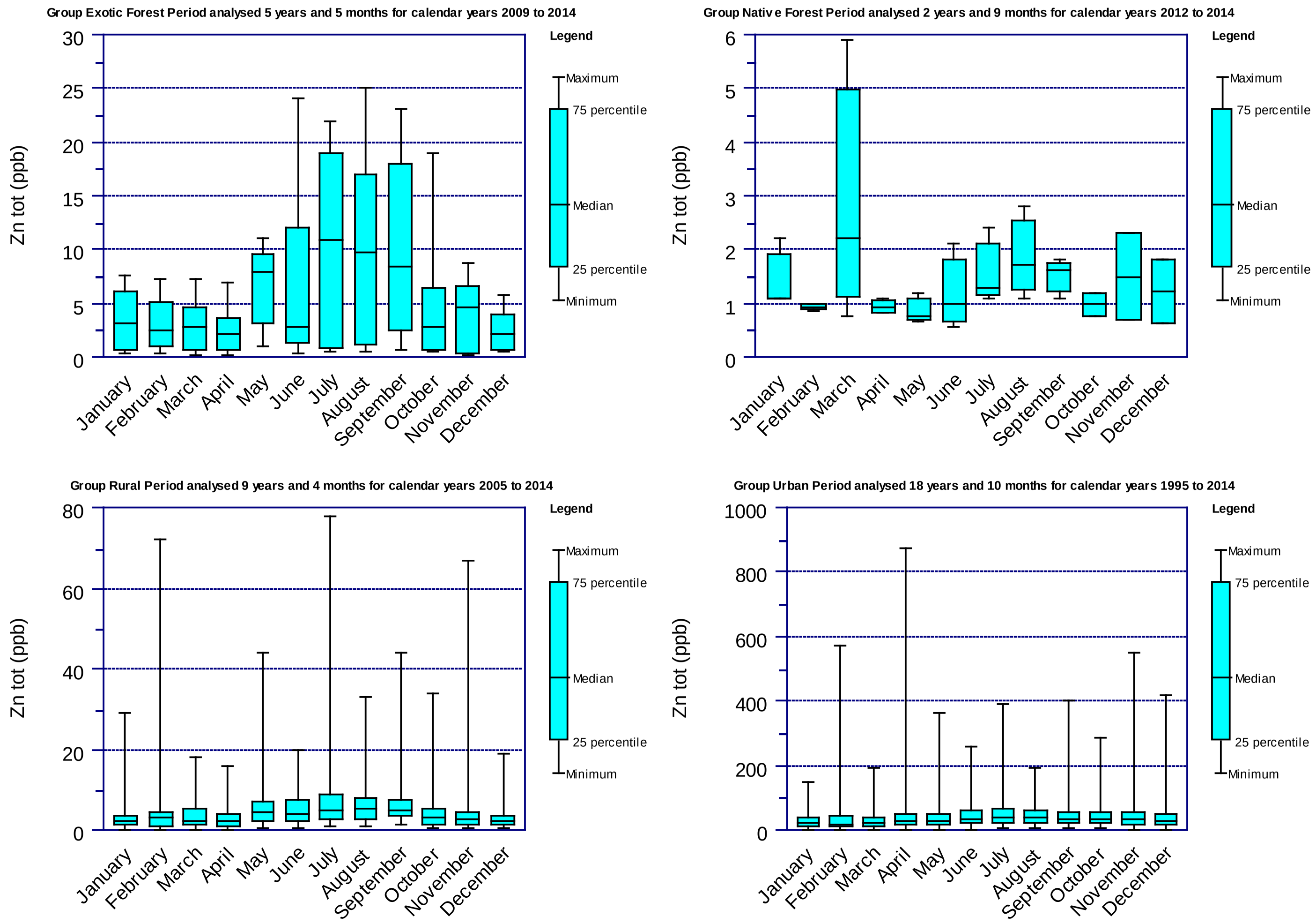


Figure D-1 Total Zn Seasonal plots

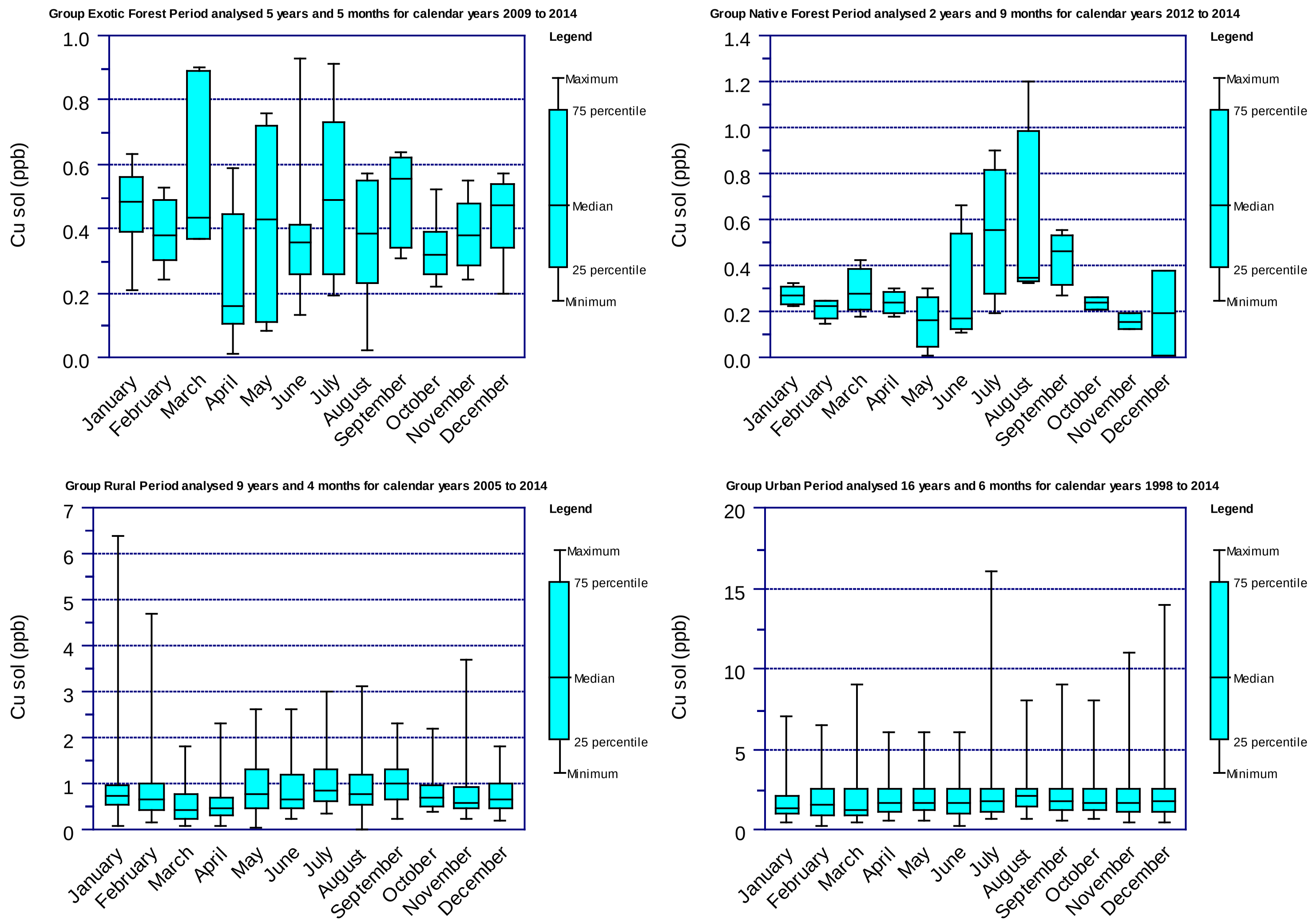


Figure 0-2 Soluble Cu Seasonal plots

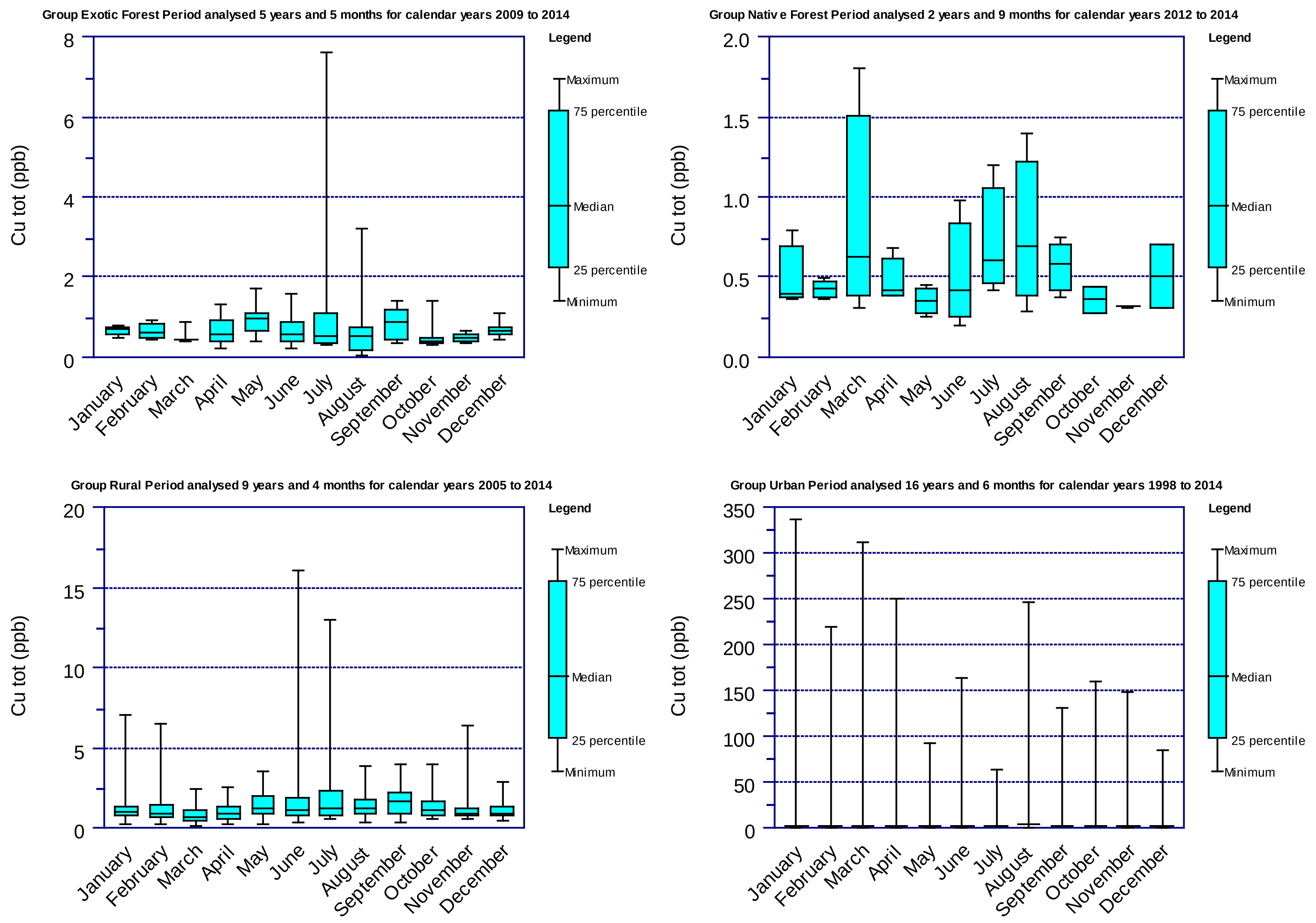


Figure D-3 Total Cu Seasonal plots

Appendix E: Twin Streams Study

Monitoring was conducted over the summer 2003/4 and 2005/6 periods and included:

- pressure monitoring, including land use (including impervious area, roading etc), potential sources of contamination (wastewater overflows, stormwater discharges), and treatment
- aquatic ecology and habitat quality assessment
- stream water quality monitoring
- stream sediment quality monitoring, and
- estuarine sediment quality monitoring.

Flow data were not recorded at each monitoring site, but the ARC flow recording data from the Opanuku, Oratia, and Swanson Streams were used to assess whether each sampling date was likely to have been affected by high flows. Figure E-1 shows the sampling dates for the 2005/6 monitoring overlain on the stream flow record from the ARC sites.

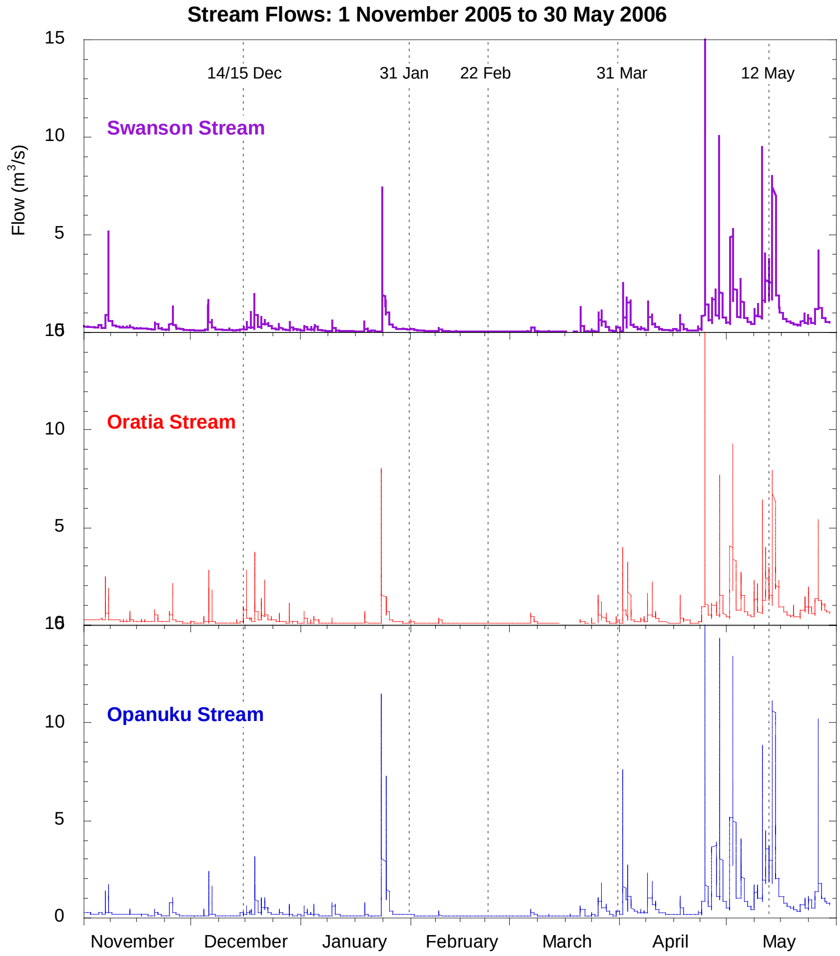


Figure E-1 Stream flows in the Twin Stream catchment for the summer of 2005/6, with water quality monitoring dates overlain (from Diffuse Sources 2006).

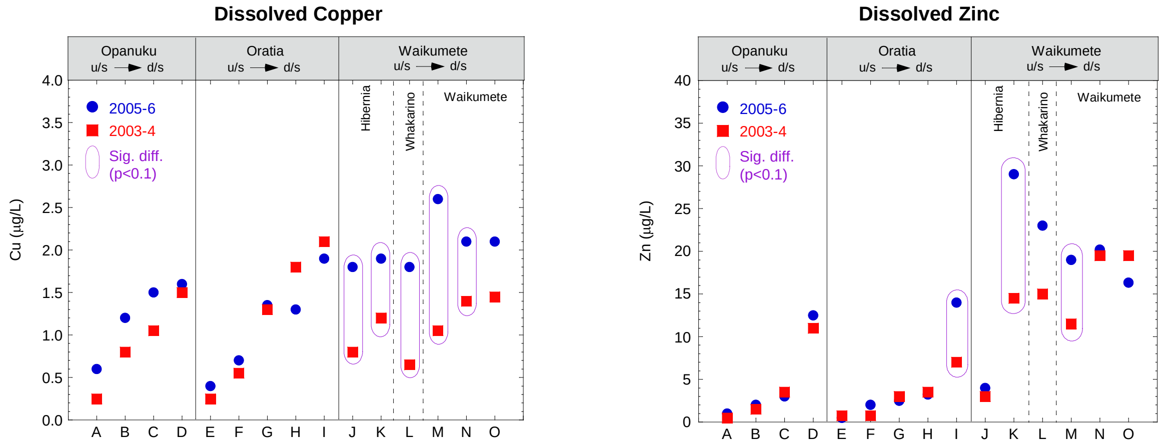


Figure E-2 Comparison of monitoring results from 2003/4 and 2005/6. Values plotted are medians from each summer (from Diffuse Sources 2006).

An assessment of the relationship between catchment “pressures” – e.g. numbers of wastewater overflows, numbers of stormwater outlets, impervious area, traffic densities – and water quality was also undertaken (Diffuse Sources 2005). In relation to metals in stream waters, a strong correlation between dissolved Zn concentrations and catchment imperviousness was found (Figure E-3). The relationship was more complex for Cu, and varied considerably between the streams. The relatively high Cu concentrations at low imperviousness may reflect the high background Cu concentrations associated with horticultural rural land use in the catchment. Imperviousness was found to be well correlated with other pressure indicators, and therefore provided a useful overall indicator of catchment pressures in the Twin Streams system.

Based on the initial pressure analysis and summer 2003/4 monitoring results, the median dissolved Zn concentrations were above the ANZECC 95% protection level (8 ppb) at approximately 10-20% imperviousness, and at the 90% protection level at around 25-30% imperviousness. The 80% protection level (31 ppb) was above the median concentrations at all sites. Note that this report used median concentrations – if 95 percentile concentrations were used the imperviousness threshold would be much lower.

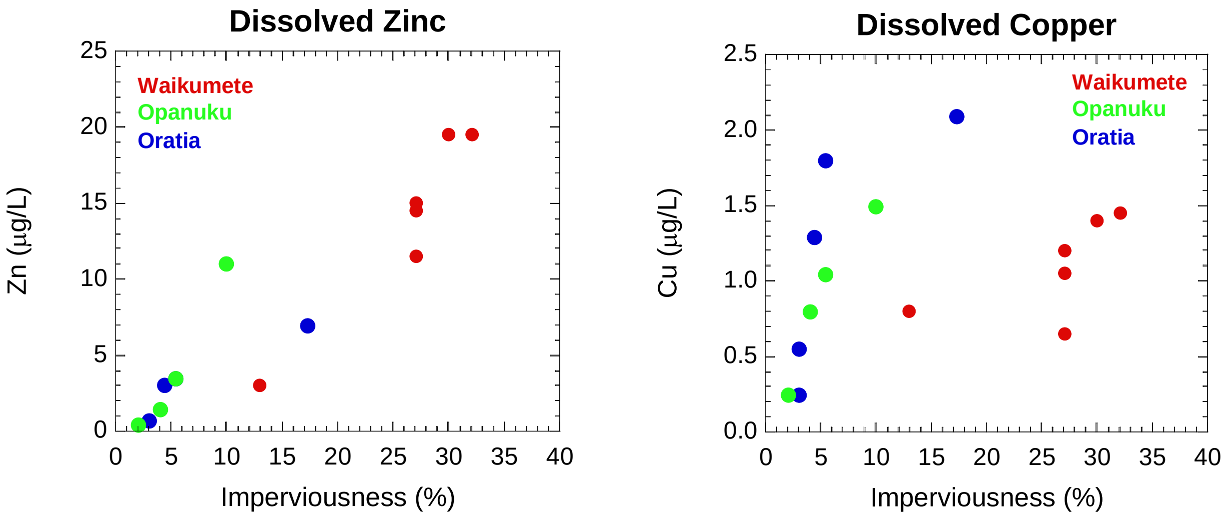


Figure E-3 Relationships between dissolved Cu and Zn (median concentrations from summer 2003/4 monitoring) and catchment imperviousness (from Diffuse Sources 2005).

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