Metal toxicity modifying factors

Relevance for the Freshwater Management Tool

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Executive summary

This report was commissioned by Healthy Waters (Auckland Council) as part of ongoing review and continuous improvement in the Freshwater Management Tool (FWMT) programme. Information and recommendations provided in this report are for the purpose of advancing the FWMT as a key decision-making and reporting tool for water quality across the Auckland region.

Auckland Council (AC) have developed the FWMT, a process-based model to predict water quality, including concentrations of zinc and copper, in their freshwater environments. The model assists with decision making and in meeting the council's obligations under the National Policy Statement for Freshwater Management (NPS-FM) by comparing predicted concentrations to compulsory numeric attributes and additional attributes of ecosystem health and human health. Attributes for copper and zinc are not mandatory nor explicitly included within the National Objective Framework (NOF) of the NPS-FM. However, AC has identified that both metals can be important stressors in freshwater and coastal receiving environments in the region.

AC published provisional zinc and copper attribute guidance as a discussion paper in 2019 (Gadd et al., 2019). The draft numeric attribute states (based on ANZECC (2000) guideline values) were used by AC in their FWMT baseline regional water quality assessment (Healthy Waters 2020b). The Australia and New Zealand (ANZ) water quality guidelines for copper and zinc are undergoing revision. Revised ANZ guidelines are expected to deal with metal bioavailability in a more sophisticated manner, by accounting for toxicity modifying factors (TMFs) in a different way to the current guidelines (which have a hardness-adjustment for zinc but no adjustments for copper).

This report specifically explores a range of TMFs that are increasingly likely to become important in determining the potential toxicity from dissolved zinc and copper exposure in Auckland's freshwater environments. The FWMT programme requested NIWA assist in preparing for updated guidance on zinc and copper freshwater toxicity, specifically:

1. to provide information on the likely requirements for TMFs in future water quality guidelines,
2. to review available information on those TMFs in relation to stream flow and other factors, including the major watersheds (as used in the FWMT) and assess gaps, and
3. to provide recommendations on how the information from objectives 1 and 2 may be accounted for in further developments of the FWMT, and to guide the design of targeted monitoring programmes.

Copper and zinc toxicity is modified by water chemistry, through changes in chemical speciation (forms of metals), and through changes in the way these metals interact with biota. The toxic forms of copper and zinc are generally considered to be the "freely dissolved" forms and some simple inorganic ions, whereas metals that are particulate bound or dissolved but attached to complex organic ligands are generally considered to be non-toxic. In waters with high concentrations of suspended sediments, or dissolved organic matter, or carbonates, there is a lower proportion of metals in the "freely dissolved form". Water hardness (a function of calcium and magnesium concentrations) influences aquatic toxicity via competition between these cations and metal cations for binding sites on biota (such as on fish gills). pH influences both speciation (through changes in metal form) and toxicity (through competition). Based on these effects on speciation and toxicity, the key TMFs that are included as part of ANZ metal water quality guidelines are pH, hardness and

Dissolved Organic Carbon (DOC, as a measure of dissolved organic matter). All three TMFs are likely to be incorporated into future ANZ zinc water quality guidelines, whilst future ANZ copper guidelines are likely to use DOC only.

A considerable amount of data regarding the TMF concentrations (or levels) in Auckland streams has been collected through State of the Environment monitoring (monthly water quality monitoring). TMF data is available at 34 sites, with pH monitored from inception at each site, and DOC and hardness monitoring initiated in November 2017 ("SOE data"). Analysis of SOE data indicates that TMFs vary both between streams and over time, although this variation is less pronounced for pH, which has a relatively narrow range within Auckland's rivers and streams (median 6.5 to 7.6). Apparent differences between major watersheds in terms of TMF concentrations correspond to differences in land use between watersheds. Streams with urban land use in their catchment typically have higher hardness than other streams, likely due to the weathering of concrete surfaces in the catchment, although there are individual urban streams with relatively low hardness (< 50 mg $CaCO_3$/L). Hardness is negatively correlated to flow in many of the Auckland streams, with lower hardness observed at higher flows (i.e., dilution during runoff events). DOC varies considerably between streams (and over time for some streams), with lower DOC in streams draining native forests and higher DOC in streams with rural and urban land use in their catchment, though there remains considerably variation (greater than a factor of two) between streams within all land use groups. Seasonal or flow-related variation in DOC is significant at relatively few sites.

The variation in TMFs between sites and over time is of an order to markedly influence toxicity and therefore water quality guideline values. Thus, we recommend that TMF variation is better represented in updated versions of the numeric attribute state reported from the FWMT to improve understanding of metal toxicity across the region. This could be undertaken through:

A. Categorising streams based on catchment land use / land cover, or other factors such as impervious surface area.

B. Categorising predictions based on the flow (baseflow or high flow).

C. Predicting TMF concentrations at each modelled reach / time-step.

We recommend that additional information (e.g., impervious surface area of catchments) be collected for each of the existing SOE sites to enable further investigation of the factors influencing TMF concentrations. We also recommend that a specific monitoring programme be designed so that data are available for TMFs over the range of flows likely to occur. This monitoring programme will expand information derived from SOE monitoring, which was intended to meet different objectives.

1 Introduction

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

The FWMT programme includes development of a continuous, process-based water quality model that covers all the Auckland region's freshwater catchments, from headwaters to coast inclusive of all rural and urban areas. The FWMT model ("FWMT") simulates processes that generate, transport, and affect the fate of contaminants (sediment, nutrients, metals and faecal indicator bacteria) from land to water using US EPA base models (Healthy Waters 2020a). This includes the simulation of total copper and zinc within streams on a continuous (15-minute) basis from 5,465 sub-catchments. The FWMT simulates copper and zinc in total forms only – post-processing is used to estimate dissolved metal concentrations.

FWMT in-stream predictions (time-series) are queried to generate concentration-based reporting measures for compulsory attributes (under the NPS-FM) and additional provisional attributes for freshwater quality state (i.e., linked to Te Mana o te Wai or human/ecosystem health values). Copper and zinc are examples of "provisional" attributes that currently have no statutory obligation for objective or limit-setting, reporting or management under the NPS-FM. However, numerous studies have demonstrated that metals are key contaminants of receiving waterways in urban areas (e.g., Williamson and Mills (2009), Milne and Watts (2008), Gadd et al. (2020)). Healthy Waters recognises the potential need therefore for copper and zinc-based decision-making under the NPS-FM. For instance, draft numeric attribute states were proposed as a discussion point for further development (Gadd et al. 2019b) and used in the AC FWMT baseline (2013-2017) regional water quality assessment (Healthy Waters 2020b). Those numeric attribute states were based on the Australian and New Zealand guidelines for fresh and marine water quality (ANZG 2018), which at that time adopted the ANZECC (2000) guidelines. This included a hardness adjustment for zinc, and no adjustment of copper to account for water chemistry.

In the AC FWMT current state assessment (Healthy Waters, 2020), predicted concentrations of dissolved copper and zinc were compared to those numeric attribute states (Table 1-1) to grade each river reach. The numeric attribute states for zinc were adjusted for water hardness, using the equations provided within ANZG (2018) and Warne et al. (2018). Three sets of numeric attribute states were derived for zinc, based on an analysis of long-term and median (baseflow) difference in hardness observed across major watersheds. Three groups of watersheds were identified as having statistically differing median hardness (based on the limited data set available at that time 2018-2020), and conservatively adjusted using the 25th% hardness as follows:

- Wairoa watershed - lowest hardness, 25th percentile of 19.2 mg $CaCO_3$ /L used to adjust guideline values,
- Tamaki watershed - highest hardness, 25th percentile of 64.4 mg $CaCO_3$ /L used to adjust guideline values, and
- streams in all remaining watersheds - 25th percentile of 38.3 mg $CaCO_3$ /L used to adjust guideline values.

Table 1-1: Numeric attribute states used for dissolved copper and zinc in the FWMT Stage 1 current state assessment. From Healthy Waters (2020).

Attribute grade	Statistic	Dissolved copper (µg/L)	Dissolved zinc (µg/L)		
			Wairoa watershed 19.2 mg $CaCO_3$/L	Tamaki watershed 64.4 mg $CaCO_3$/L	Regional† 38.3 mg $CaCO_3$/L
A	Median	≤ 1	≤ 1.7	≤ 4.6	≤ 2.9
	95th percentile	≤ 1.4	≤ 5.6	≤ 15.2	≤ 9.6
B	Median	> 1 and ≤ 1.4	> 1.7 and ≤ 5.6	> 4.6 and ≤ 15.2	> 2.9 and ≤ 9.6
	95th percentile	> 1.4 and ≤ 1.8	> 5.6 and ≤ 10.5	> 15.2 and ≤ 28.5	> 9.6 and ≤ 18.0
C	Median	> 1.4 and ≤ 2.5	> 5.6 and ≤ 21.7	> 15.2 and ≤ 58.9	> 9.6 and ≤ 37.2
	95th percentile	> 1.8 and ≤ 4.3	> 10.5 and ≤ 29.4	> 30.0 and ≤ 79.8	> 18.0 and ≤ 50.4
Regional bottom line					
D	Median	> 2.5	> 21.7	> 58.9	> 37.2
	95th percentile	> 4.3	> 29.4	> 79.8	> 50.4

Note: † Regional category covers all streams not in the Wairoa or Tamaki watersheds.

Future versions of both the copper and zinc guidelines are expected to account for the factors that modify metal bioavailability and toxicity (referred to in this report as toxicity modifying factors, or TMFs), and in a different way to a simple hardness adjustment. Therefore, future numeric attribute states reported by the FWMT may also need to consider these factors to more accurately assess potential toxicity from copper and zinc in freshwater environments.

This project was conceived for and funded by the FWMT programme (Healthy Waters), with three primary objectives:

1. Provide commentary on likely requirements for toxicity modifying factors in future water quality guidelines for New Zealand.
2. Review available data on TMFs, including in relation to stream flow and other factors, and assess gaps in information.
3. Provide recommendations on how these findings may be considered during further development of the FWMT and in targeted monitoring programmes.

This report is set out as outlined below.

- Section 2 describes how water chemistry modifies metal toxicity through chemical speciation and interactions with biota, and describes models used within water quality guidelines to account for TMFs.
- Section 3 focuses on the key TMFs identified in section 2 and presents information on how these vary spatially and temporally (including with flow). This information is largely based on analysis of data collected through routine monitoring in AC's State of the Environment (SOE) programme, supplemented with additional data from around Aotearoa New Zealand.

- The implications section (section 4) pulls the information from sections 2-3 together in the context of the FWMT. It makes recommendations about how TMFs may be considered in future iterations of the FWMT.

2 Metal water quality guidelines and toxicity modifying factors

2.1 Introduction

Metal toxicity depends on both the concentration of metals in the aquatic environment and their bioavailability. Bioavailability, as most recently defined by Adams et al. (2020), is "a measure of the rate and extent to which a toxic substance reaches the toxic site of action". Factors that limit bioavailability include the solubility of a toxicant; their sorption to particulate or colloidal material or dissolved organic matter; chemical speciation; and the presence of chemicals that compete for binding sites (Adams et al. 2020, Allen & Hansen 1996, Campbell 1995). Some of these factors can be accounted for through analytical methods whilst others can be accounted for using chemical speciation models. However, bioavailability models are required to incorporate both the abiotic and biotic influences on bioavailability as this is not just influenced by the metal and water chemistry but also by biological organisms, with different effects between different types of organisms (and different species).

This chapter covers, firstly, the influence of both chemical speciation (section 2.2) and biotic interactions (section 2.3) on metal toxicity; then presents bioavailability models commonly used to account for toxicity modification including those used within the water quality guidelines (ANZG 2018) used in New Zealand (section 2.4).

2.2 Water chemistry affects chemical speciation

Metals in solution may be found in numerous forms, including those that are adsorbed to, or bound within the sediment matrix, those that are "dissolved", as well as different ionic forms, and for some metals, different oxidation states (Figure 2-1).

Metals readily bind to suspended particles, particularly fine sediments which have high surface area, and clay particles which have negatively-charged binding sites. Although these adsorbed or bound forms of metals may be available to some organisms through feeding (e.g., filter feeders), they are not readily bioavailable through water uptake, which is the primary route for aquatic toxicity. Total recoverable measurements of metals use a strong acid digestion, which can dissolve metals adsorbed to solids, and to an extent, even elemental copper, lead and zinc. Water quality monitoring data derived from methods of analysis that include strong acid digestion therefore typically over-estimate the bioavailable concentrations of metals.

For assessing ecotoxicological effects, the dissolved form of metals provides a better measure of the bioavailable fraction because the metals adsorbed to particulate matter are not included in this measurement (USEPA 1996, Warne et al. 2018). However, the definition of dissolved metals is procedural, that is, the metals present in a solution after passing through a 0.45 µm pore size filter. Despite the term, some of the metals reported as "dissolved" are not truly dissolved and are attached to colloidal material (Stumm & Morgan 1996). In addition, nano forms of metals, such as engineered nanoparticles like zinc oxide, which are not dissolved can also pass through these filters because of their very small (nm) size. At this stage, it is still unclear whether metal nanoparticles exert toxic effects on aquatic organisms (Du et al. 2020, Ma et al. 2013).

Colloids (substances 1,000 Dalton[1] to 0.1 µm in size) include humic substances such as humic and fulvic acids, which can be derived from terrestrial sources, such as peat soils or leaf litter, and from aquatic sources such as green algal production. Metal ions readily bind to such materials, especially copper, which competes with proton ions in binding to carboxylic, phenolic and hydroxyl groups; the extent of this complexation depends on the presence of competing ions and on pH (Stumm & Morgan 1996). Humic substances are considered too large to be taken up by most organisms and hence metals attached to such substances are considered to be of low bioavailability (Campbell 1995).

Of the dissolved metals, there can be many different chemical species – for example copper can be present in one of two oxidation states – either Cu(I) or Cu(II). However, the cuprous ion (Cu^+) is unstable in aqueous media and will oxidise to the cupric form (Cu^{2+}). Although this cupric form can be found in solution as "free copper" (although more correctly as $Cu.nH_2O^{+2}$), the majority is found as inorganic complexes in natural waters, such as oxides (e.g., CuO), hydroxides ($CuOH^+$), carbonates and bicarbonates ($CuCO_3^+$, $CuHCO_3^+$). Although zinc also has more than one oxidation state, it is invariably found in the +2 oxidation state (Zn(II)), and like copper, can exist as the free zinc form (Zn^{2+}) and as multiple inorganic ions when in solution ($Zn(OH)^-$, $Zn(OH)_4{}^{2-}$, see Figure 2-1). These inorganic ions (also called salts) have differing solubility, for example, $CuCO_3$ is much less soluble (solubility 0.0014 g/L) than $CuSO_4$ (320 g/L). Importantly, the metal salts can also have differing toxicity: for copper the most toxic forms are Cu^{2+}, $CuOH^+$ and potentially $Cu_2(OH)_2{}^{2+}$; carbonate forms are considered to be non-toxic (Allen & Hansen 1996).

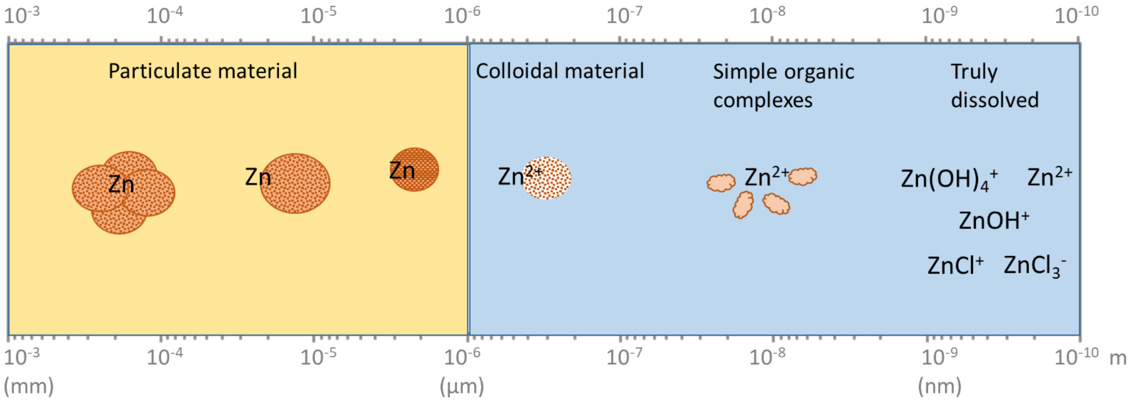

Figure 2-1: Particulate, colloidal and dissolved forms of zinc in a freshwater system. Tan colour background indicates particulate phase, while blue indicates dissolved phase, based on filtration through filters with pore size 0.45 µm.

The relative distribution of zinc and copper amongst the different chemical species is dependent on pH, the oxidation-reduction potential in the local environment, and the presence of competing metal ions and inorganic anions (Stumm & Morgan 1996). For example, for zinc at pH 4-7 the free zinc ion (Zn^{2+}) is by far the most dominant of dissolved forms (see Figure 2-2), while at pH 8-9 $ZnCO_3$ also becomes important (Stumm & Morgan 1996). Hydroxide forms are less prevalent and chloride complexes are insignificant (Stumm & Morgan 1996). Although complexation to organic ligands, such as humic acids, is not highly significant for zinc, zinc does however partition to suspended particulate

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[1] A unit of mass, commonly used for small particles, proteins and polymers

matter in oxidized neutral to alkaline environments (Stumm & Morgan 1996). By contrast, for copper at pH > 6.5 the free species (Cu^{2+}) is usually a very small percentage of the dissolved copper (Stumm & Morgan 1996) and typically over 90% of the dissolved form is found bound to inorganic or organic ligands such as humic acids, fulvic acids, hydroxides, carbonates, and other inorganic ligands, which are much less toxic than the free cupric ion (Van Sprang et al. 2008a). In natural waters, the organic ligands are the most important (Stumm & Morgan 1996) and complexation with dissolved organic matter (DOM) increases as the pH and concentration of DOM are increased, and as the concentrations of competing ions are decreased (Stumm & Morgan 1996). The speciation of dissolved copper and zinc are therefore both dependent on specific aspects of water chemistry, such as the pH and concentrations of humic acids and carbonates, and, as such, the toxicity of these metals will vary between water bodies that vary in these aspects.

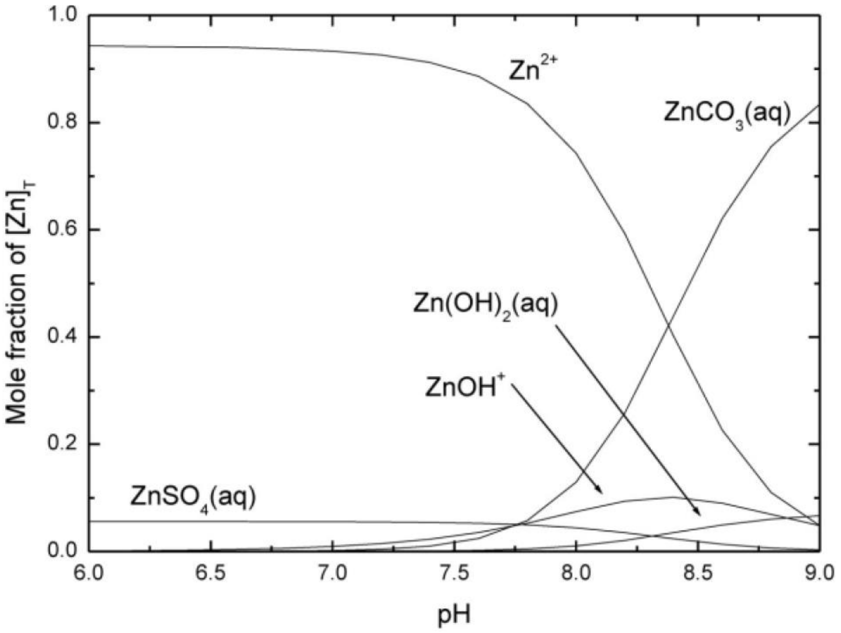

Figure 2-2: Speciation diagram for zinc in a simulated freshwater medium. Figure from Powell et al. (2015). Freshwater system includes Zn^{2+}, H^+, Cl^-, CO_3^{2-}, SO_4^{2-} and HPO_4^{2-} ions and carbonato- and sulfato- complexes of Mg^{2+} and Ca^{2+} (not shown).

The speciation of metal ions can be modelled using equilibrium models such as MINTEQ (combining MINEQL and WATEQ3; Allison et al. 1991, Brown 1987), WHAM (Windermere Humic Aqueous Model; Tipping & Hurley 1992) and PHREEQC (pH-REdox-EQuilibrium model in C++;Parkhurst & Appelo 2013). Inputs to these models include pH, water temperature, alkalinity and the concentrations of DOC, major cations and anions and key metals like iron and aluminium. These models incorporate the four main types of chemical reactions determining metal speciation, (Bourg, 1995): adsorption and desorption processes; ion exchange and dissolution reactions; precipitation and co-precipitation; and complexation to inorganic and organic ligands. Each of these models simulate speciation based on equilibrium constants that are derived from laboratory experiments, but each model differs somewhat in the way they model organic matter and solid phase interactions.

Metal speciation can also be measured using a range of different laboratory methods such as voltammetry, ion selective electrodes, ion-exchange column techniques, and hyphenated techniques such as GC-ICP-MS or HPLC-ICP-MS (Han & Pan 2021, Krupp et al. 2005, Tipping et al. 2016). There are also several in situ methods including DGTs (diffusive gradients in thin-films), Donnan membrane technique (DMT) and Permeation liquid membranes (PLM) (Hamilton-Taylor et al. 2011). These methods typically measure either the “free” metal ions, or the labile components, which relate closely to the bioavailable fraction (Degryse & Smolders 2016, Jolley et al. 2016). With the exception of DGTs, these are specialised techniques used in research laboratories and are not available for routine monitoring. DGTs on the other hand are becoming widely available and have been used in and recommended for regulatory monitoring in NZ (Gadd & Milne 2019). DGTs are also widely accepted as a method to measure bioavailable metals and are one of the methods recommended by ANZG (2018) to determine bioavailable metals for comparison to default guideline values.

2.3 Water chemistry affects aquatic toxicity

The effect of different TMFs on aquatic toxicity has been investigated in toxicological tests beginning as far back as the 1960s and 1970s (Meyer et al. 2007, Sprague 1985). At that time researchers recognised that in addition to the effect of inorganic anions and organic matter on metal speciation, metal toxicity was also influenced by water hardness and pH, and then determined that this was because of competition from calcium and H^+ ions, not changes in metal speciation (Adams et al. 2020, Meyer et al. 2007). Since then, there have been numerous investigations into the effect of different toxicity modifying factors on a range of different aquatic organisms, in both acute (short-term, often lethal) and chronic (long-term, usually sub-lethal) toxicity tests. Many of these studies were included in a comprehensive review by Meyer et al. (2007) of the effects of water chemistry on the acute and chronic toxicity of five cationic metals (cadmium, copper, nickel, lead, and zinc). The rest of this section looks at different TMFs and their effects on metal toxicity (which incorporates both speciation effects and those that occur within an organism), focussing on copper and zinc.

2.3.1 Dissolved Organic Matter and Dissolved Organic Carbon

Dissolved organic matter (DOM, usually measured as organic carbon, thus DOC) affects zinc toxicity primarily through formation of metal complexes which are of low bioavailability, thus reducing the toxicity of metals in waters with high DOC. This effect has been reported for many test organisms (as reviewed in Meyer et al. (2007)), including: fish (rainbow trout, fathead minnow), invertebrates (e.g., water fleas) and even algae (De Schamphelaere et al. 2005a). Acute and chronic tests with key test species such as rainbow trout, fathead minnows and waterfleas indicate that DOM reduces metal toxicity (Meyer et al. 2007). The same effect has also been shown for Australasian species. For example, the acute toxicity of copper and zinc to native New Zealand freshwater snails (*Potamopyrgus antipodarium*), amphipods (*Paracalliope fluviatilis*), and water fleas (*Daphnia thomsoni*) has been demonstrated to be lower in the presence of organic matter derived from native plants (Thompson et al. 2019). The same effect has since been demonstrated in chronic toxicity tests with the native water flea (NIWA, unpublished data).

Not all metals are influenced by DOM - Markich et al. (2003) reported that DOC modified toxicity of copper to freshwater mussels (*Hyridella depressa*), but not of cadmium. Similarly, the influence of DOC on zinc toxicity is lower than on copper toxicity, and appears to be strongest in waters of soft to moderate hardness (< 200 mg/L as $CaCO_3$, (Winner & Gauss 1986)), and generally at DOM concentrations > 5-10 mg/L (Meyer et al. 2007). These effects are probably due to the weak affinity of zinc to DOM relative to copper (Stumm & Morgan 1996). As the mechanism by which DOM reduces toxicity is generally considered to occur through speciation and to be consistent across aquatic species, metal speciation modelling can be used to account for the influence of DOM on metal toxicity.

2.3.2 Water hardness

The influence of water hardness (the amount of dissolved calcium and magnesium in water) on metal toxicity has been studied extensively. The aquatic toxicity of metals can decrease as water hardness increases due to competition between metals and calcium (and to a lesser extent, magnesium and sodium) cations for binding sites on biological tissues such as fish gills (Bradley & Sprague 1985, Heijerick et al. 2002). This competition for binding sites occurs for several cationic metals in algae, invertebrates and fish, and in both acute and chronic toxicity tests, though there are far more data documenting this relationship in acute tests. An example from chronic tests includes a study with the water flea *Daphnia magna*, where a 4-fold increase in hardness decreased zinc toxicity 6-fold (Paulauskis & Winner 1988). For brown trout (*Salmo trutta*), increases in hardness from 37 to 200 mg/L (factor of 5) resulted in increases in the LC_{50} values (concentrations lethal to 50% of organisms) from ~1000 µg/L to ~2300 µg/L (factor of 2) (Davies & Brinkman 1999); similar results have been reported for rainbow trout (*Oncorhynchus mykiss*) and Colorado River cutthroat (*Oncorhynchus clarkii pleuriticus*) (Brinkman & Hansen 2004). For copper, the effect of water hardness is less clear. Hardness appears to reduce copper toxicity to fish species, especially in acute tests (e.g., rainbow and bull trout, or see reviews (Allen & Hansen 1996, Campbell 1995, Hunt 1987, Paquin et al. 2002)). However, this effect is not consistent across all organisms: several studies have demonstrated no effect of hardness on water fleas (De Schamphelaere & Janssen 2002, Hyne et al. 2005, Markich et al. 2005); macrophytes (Markich et al. 2006) and green algal species (De Schamphelaere et al. 2003, Markich et al. 2005).

2.3.3 pH

The pH of a waterbody affects metal toxicity through antagonistic mechanisms: firstly, influencing metal speciation, resulting in increased concentrations of bioavailable metal species at lower pH (increasing toxicity at low pH); and secondly, by the H^+ ion competing with metals in binding to biotic ligands (decreasing toxicity at low pH). This can result in contradictory effects of pH on aquatic toxicity depending on species and test. In their meta-analysis of chronic copper toxicity data, Meyer et al. (2007) found positive correlations between pH and chronic toxicity values (meaning toxicity decreased as pH increased) that were statistically significant for fathead minnows, marginally significant for one species of water flea (*D. pulex*), but not significant for a second species (*D. magna*). In contrast, for tests involving *D. magna*, and for a freshwater algal species, the toxicity of copper decreased as pH decreased (De Schamphelaere & Janssen 2004, De Schamphelaere et al. 2005b), consistent with the competition mechanism.

Zinc toxicity to rainbow trout and *D. magna* decreases as pH decreases, which by measuring or modelling the concentrations of free zinc, has been attributed to competition between H^+ and zinc ions (Heijerick et al. 2005, Van Regenmortel et al. 2017). Similar results have been observed for two different freshwater algal species (Price et al. 2021, Van Regenmortel et al. 2017).

2.3.4 Alkalinity

Alkalinity (usually due to carbonate) affects metal toxicity by forming carbonate complexes with dissolved metals, thereby reducing the concentrations of free metals ions (a speciation-mediated effect). In general, studies have shown lower toxicity at higher alkalinity, for both copper and zinc and in acute and chronic tests. However, in many cases the hardness of the water and/or the pH vary alongside the alkalinity, and it is not clear whether changes in toxicity are attributable to alkalinity, other characteristics, or combinations of these. Of the few studies that compared alkalinity while maintaining constant water hardness, two showed alkalinity had no influence on zinc toxicity to rainbow trout at or below pH 7 (Barron & Albeke 2000, Bradley & Sprague 1985), whilst a third study suggested that both hardness and alkalinity were important influences on zinc toxicity to rainbow trout and brook trout (Holcombe & Andrew 1978).

2.3.5 Temperature

Water temperature can potentially affect metal toxicity due to increased metabolic rates and increased respiratory inflows (Khangarot & Ray 1989). Correlations between metal toxicity and temperature have been observed for several species, with higher toxicity at higher water temperatures, though this correlation is less apparent in chronic tests (Meyer et al. 2007, Van Sprang et al. 2008b).

2.4 Accounting for TMFs in water quality guidelines

The effects of TMFs on aquatic toxicity have been considered when developing water quality guideline values since the 1970s; as a consequence, guidelines have become increasingly complex over time. In New Zealand, TMFs have been considered since 2000 within the ANZECC/ARMCANZ (2000) guidelines, and are also incorporated into the total ammoniacal-nitrogen attributes within the NPS-FM.

In 1976, the United States EPA recommended different guideline values for cadmium in soft and hard water (US EPA 1976). Guidelines developed for cadmium, copper, lead, nickel and zinc in 1980 (US EPA 1980a, US EPA 1980b, US EPA 1980c, US EPA 1980d, US EPA 1980e) used linear regressions of water hardness and acute toxicity effect concentrations to develop equations to adjust criteria at different hardness levels, based on the slope of that regression. For all metals, the criteria are higher at higher hardness levels. For example, the equation for the copper criteria is:

$$\text{Criterion continuous concentration} = e^{(0.8545[1n(hardness)]-1.465)}$$

The ANZECC/ARMCANZ (2000) guidelines for the metals listed above adopted the same slopes as used in the US EPA derivations, although these were applied to different guideline values that were derived following the ANZECC/ARMCANZ procedure.

In the 1980s and 1990s, the free-ion activity model was developed, which describes interaction of living organisms with free metal ions (e.g., Campbell 1995), similar to a metal speciation model. The gill-surface interaction model was also proposed (Pagenkopf 1983), which modelled metal binding to gills and accounted for competition by cations. These two models were later developed into the biotic ligand model (BLM), which essentially predicts metal accumulation on fish gills (or any other biological ligand) of an aquatic organism (Di Toro et al. 2001). The BLM incorporates the influences of toxicity modifying factors on both speciation (including complexation by natural organic matter using WHAM) and competition at the biotic ligand. The full biotic ligand model requires site-specific concentrations of ten factors: temperature, pH, DOC, calcium, magnesium, sodium, potassium, sulfate, chloride, and alkalinity. The BLM then uses mathematical algorithms to calculate either the concentration of a metal that would result in toxicity at that point in time, or a BLM-based water quality guideline value based on those input values[2].

BLMs are derived from laboratory-based ecotoxicity tests on a single species of aquatic organism conducted with different concentrations of the factors (pH, calcium etc) that influence toxicity.

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[2] The BLM can also be run in speciation mode, where it calculates the speciation of the metal of interest based on the input water chemistry.

Although originally based on acute toxicity data for rainbow trout and fathead minnows, the model (or model framework) has been extended to invertebrates and algal species, and to chronic toxicity data. Several discrete BLMs are required to describe the bioavailability of a metal across several trophic levels i.e., fish, invertebrates and algae.

Biotic ligand models have been promoted as a method to account for the effect of water quality modifiers, and form part of the method to calculate varying water quality guideline values for copper in the United States (US EPA 2007), Canada (ECCC 2021). BLMs were also used in the European copper risk assessment (European Copper Institute 2008) and recommended for use in a European guideline. Each of these BLMs differs in the model coefficients used, depending on the organism/species the model is based on, and whether based on acute or chronic toxicity data. The copper BLM used in the US is based on acute toxicity data for several fish and invertebrate species (US EPA 2007). In contrast, the Canadian BLM is based on chronic toxicity data for fish, invertebrates and algae (ECCC 2021).

BLMs have also been developed for a wide range of other metals including zinc, nickel, lead, silver and cadmium, each using a specific set of toxicity data. These BLMs are used globally in metal water quality guidelines. Biotic ligand models have not yet been used in the ANZG (2018) water quality guidelines though their application was investigated in the derivation for nickel in freshwaters (Peters et al. 2021).

The disadvantages of the BLM approach are considered to be the complexity - requiring data for water quality variables not routinely analysed in monitoring programmes – and that the software is not considered particularly user-friendly for regulators (Verschoor et al. 2012). This led to the development in Europe of several “user-friendly” BLM tools such as Bio-met, PNEC-pro, and MBAT (Ten Hulscher et al. 2021). These tools either use look-up tables developed from multiple BLM runs or simplified algorithms to predict bioavailable metals more rapidly and with fewer input variables – the required variables being only DOC, pH and hardness or calcium. These methods have not been proposed for use in Australia / New Zealand guidelines. However, the main BLM software provider (Windward Environment) has since been updated the programme to allow for “simplified site chemistry” to be used – based on only temperature, pH, DOC and hardness (Windward Environmental 2019), removing the requirement to measure multiple additional water quality variables. A simplified version (as well as the detailed) is available for calculating the Canadian water quality guideline for copper.

As the inputs to the model represent a single point in time, the result is an indication of the bioavailability and toxicity or the guideline value (in the case of BLMs incorporated into water quality guidelines) only at that point in time. Multiple points in time can be modelled by inputting multiple lines of input data. As water chemistry changes over time, and between sites, several or many different water quality guidelines may be derived at different points in time and space – a further complication when implementing a BLM-based guideline. Although this is also true of hardness-based guidelines, the difficulties arising from use of multiple guideline values was typically addressed through the use of an average or low-percentile hardness when calculating the guidelines. Such an approach is not as readily applied with the BLM because the model integrates multiple aspects of water chemistry. Using average or low-percentile conditions throughout those inputs is not considered defensible as it is unlikely that low-percentile conditions would all occur at the same time (Ryan et al. 2018).

A further limitation with the BLM approach is that all of the models have been developed based on a small number of species (typically model organisms, such as rainbow trout and the water flea *Daphnia magna*). Though the applicability of the models to other aquatic species has been validated through additional testing, there remains uncertainty around applicability to other organisms, particularly sensitive native organisms (Peters et al. 2021, Stauber et al. 2022).

An alternative approach for accounting for toxicity modifiers using multiple linear regression (MLR) models has been proposed internationally (Brix et al. 2017, Brix et al. 2020, Brix et al. 2021). This approach has been promoted by authors due to its simplicity and ease of use for regulators (Brix et al. 2020). Such models have been used in the Canadian water quality guideline for zinc (Canadian Council of Ministers of the Environment 2018), and for the proposed Australia and New Zealand (ANZ) water quality guideline for nickel (Stauber et al. 2021).

Based on international research and the developments in water quality guidelines, it is most likely that future ANZ water quality guidelines for metals will include pH, hardness and/or DOC as key toxicity modifying factors. The draft freshwater copper guideline submitted to the ANZG committee has an adjustment based on DOC only (Gadd 2021) as this was shown to be the TMF that affects toxicity the most, and is consistent across species. The zinc water quality guidelines are still in development and the specific models likely to be used to adjust for bioavailability and water chemistry are under discussion; however they are expected to incorporate pH, hardness and DOC (Stauber et al. 2022). While it is possible that BLMs may be incorporated into zinc water quality guidelines, it is likely (based on recently proposed guidelines) that simplified versions of the BLM (which require only temperature, pH, hardness and DOC) or MLRs (based on the same or a subset of these variables) would be used, similar to the proposed nickel guidelines (Stauber et al. 2021). Currently no acute guidelines for copper or zinc are in development in New Zealand; however if any are to be developed, they will most likely consider pH, hardness and DOC as key TMFs.

Current research relevant to the development of improved metal bioavailability models includes characterisation of DOM (Holland et al. 2018) and improving the understanding of how DOM binds metals (Al-Reasi et al. 2011); generalized bioavailability models (gBAMs) that can account for log-linear effects of TMFs (Nys et al. 2020), and models that account for the interaction of metal mixtures (Meyer et al. 2015). However, it is not likely that these aspects will be considered within Australia New Zealand water quality guidelines in the near future.

2.5 Summary

The speciation and bioavailability of copper and zinc (and other metals) is influenced by water chemistry, with the greatest influences being DOM (especially for copper), pH, hardness and water temperature. The effect of these TMFs on toxicity can be accounted for in multiple ways, from simple linear regressions (e.g., hardness-related criteria), to multiple linear regressions and BLMs.

The ANZ freshwater copper guidelines are not yet published however the submitted draft includes an algorithm to adjust guideline values based on DOC concentrations in the water.

The ANZ zinc guideline is still under development, but it is expected that algorithms (likely based on MLR) will be used to adjust guideline values, based on the three key TMFs of DOC, pH and hardness. Therefore, to meet the future requirements of the FWMT, consideration should be given to monitoring at least three key TMFs: DOC, pH and hardness

3 Processes influencing hydrochemistry of TMFs & evidence in NZ streams

3.1 Introduction

This chapter provides a review of the existing knowledge of the hydrochemistry of the key toxicity modifying factors (TMFs) discussed in chapter 2, namely pH, major ions (focussing on calcium and magnesium; and together as water hardness), and dissolved organic matter. Water temperature is also included as this is a key factor used in metal speciation and biotic ligand models, which may be used in understanding metal bioavailability and toxicity. The factors that influence the concentration (or level) of these TMFs in rivers and streams are discussed with evidence from monitoring in Auckland streams (primarily the SOE data set) and elsewhere around New Zealand. These factors include climate, topography, geology, land use, flow, season and time of day. The data analyses in this chapter are exploratory only, with minimal use of statistical analyses or tests to compare between groups/factors.

3.2 Data sources and analyses

A range of data sets was used in this chapter to investigate and illustrate the processes that affect TMF concentrations within rivers and streams (see summary Table 3-1). The primary source of data was AC's SOE monitoring programme, which includes monthly measurements of TMFs at over 30 sites. However, this sampling occurs routinely, at monthly intervals, and generally during low flows. It is therefore not suitable for investigating diurnal changes in TMFs, for understanding intra-event dynamics, and has limitations in improving our understanding of flow-related changes. These data were therefore supplemented with high frequency data and storm event data collected at specific sites in Auckland. Furthermore, as water hardness and DOC have only recently been added to the SOE monitoring programme, these data were supplemented with those collected throughout New Zealand rivers during national surveys (Scott et al. 2006, Smith & Maasdam 1994). These different data sets are used within the following sections depending on the TMF and the spatial or temporal extent of the processes being discussed.

As stated, stream water quality data for the Auckland region were obtained from AC's SOE monitoring programme (see Appendix A for a list of sites, including the date when sampling began). In this programme, which began in 2003, water samples were collected monthly from between 34-37 sites (the number of sites has changed slightly over the duration of the programme (see Ingley & Groom 2021, Ingley & Groom 2022)), and were analysed for a suite of water quality variables including the key TMFs. The pH of the water has been measured throughout the programme, either in the field or in the laboratory (currently both, where possible). Calcium, magnesium (and calculated hardness) and DOC (as DNPOC, dissolved non-purgeable organic carbon) were added to the list of measured variables in November 2017 for all but one (Hoteo at Gubbs) of the 34 sites currently in the programme. Of the variables required, only temperature is currently measured in the Hoteo River [3]. Streamflow is measured continuously at (or close enough to the site to represent the flow at the water quality site) at 14 of the monitoring sites where all the TMFs are monitored, and at Hoteo at Gubbs. The flow data were obtained from AC's Research Evaluation Unit (RIMU) group, and were used to examine relationships between the TMFs and flow.

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[3] Data are collected by NIWA and provided to AC for use in their reporting under a data sharing agreement.

Table 3-1: Data sources used to explore hydrochemistry of TMFs..

Name	Data type	No. sites	Duration of data	Source
AC SOE monitoring programme	Monthly discrete monitoring of temperature, pH, Ca, Mg and DOC	34-37	2003 – June 2021 [a]	Supplied by AC
Temperature data	High frequency (every 15 mins)	1	Jan – July 2022	AC's Environmental Data Portal
pH sonde data	High frequency (every 15 mins)	1	April 2022	NIWA unpublished data
DOC event-based data	Storm event	2	One event, 21-22 March 2022	NIWA unpublished data
National River Water Quality Network	Monthly discrete monitoring of temperature and pH	77	Jan 1989 - Dec 2012	https://hydrowebportal.niwa.co.nz/Data
National River Water Quality Network	Monthly discrete monitoring of anions and cations	77	Jan 1989- May 1990	Smith & Maasdam (1994)
DOC survey	Monthly discrete monitoring of DOC	52	Oct 2001 – May 2002	Scott et al. (2006)

Notes: [a] Data duration differs for each site and for the different water quality variables measured. See Appendix A for site-specific details.

Data for these variables were obtained for all data up to June 2021, covering up to 18 years for pH (depending on when the site was introduced into the programme) and a 44-month period for DOC and hardness. Each site was classified into one of four land use groups adopted from Ingley and Groom (2022): Native Forest, Exotic Forest, Rural (includes all non-forested rural land, namely pastoral and horticultural land) and Urban (Table 3-2). Each site was also categorised by the major watershed they are located within, based on the 10 watersheds used in the FWMT and associated reporting (see Healthy Waters 2020a), as shown in Figure 3-1 and listed in Table 3-2.

Table 3-2: Two categories used in exploratory data analyses. Watersheds as used in FWMT reporting (Healthy Waters 2020a). Land use categories adopted from Ingley and Groom (2022).

Watersheds	No. stream sites	Land use categories	No. stream sites
West Coast	1	Native	6
Kaipara	5	Exotic forest	2
North East	1	Rural (> 25% rural land use in catchment by area)	16
Mahurangi	2		
Hibiscus Coast	5	Urban (>15% urban land use)	11
Waitemata	6		
Islands	2		
Tamaki	5		
Manukau	6		
Wairoa	2		

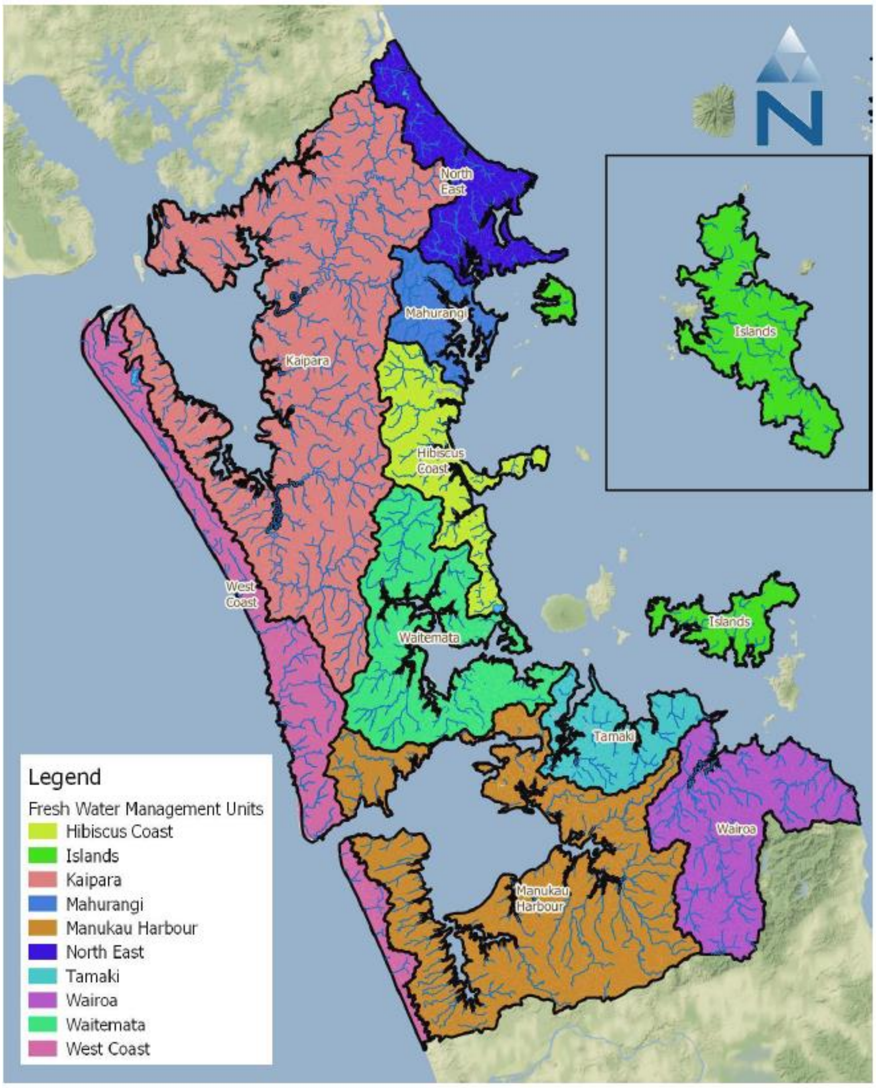

Figure 3-1: Freshwater Management Tool watersheds. Figure from Healthy Waters (2020b).

Very high flows are not well represented in the SOE monitoring data set as these flows occur infrequently and at some locations are not sampled due to health and safety concerns. This means that there are fewer measurements of the TMFs at high flows, particularly for hardness and DOC as monitoring of these started more recently and represent a reduced range of flows in the 44-month period of monitoring to date. This is shown in Figure 3-2, by comparing the flow duration curve for all flows monitored over the duration of flow monitoring (based on hourly average flows), with curves for flows represented in monitoring of pH and of hardness/DOC.

This comparison demonstrates the information gaps at very high and very low flows at most, but not all sites. For example, in the Mahurangi River (Warkworth), flows reach over 100 m^3/s, but pH has only been monitored at flows up to 29 m^3/s and hardness/DOC at flows up to 5.4 m^3/s. At the same site, the lowest flows do appear to have been sampled for pH, hardness and DOC. At the Vaughan Stream site however, the lowest flows on record (<0.00004 m^3/s) do not appear to have been sampled for pH and flows <0.0001 m^3/s have not yet been sampled for hardness/DOC. This implies that statistical summaries of hardness and DOC (and to a lesser extent pH) based on the measured data may not represent the full spectrum of flows over which metals are modelled in the FWMT. Note however that these figures are for the full flow data series for each site, which in most cases is much greater than the 5 years modelled by the tool. On the other hand, it is clear from the overlapping lines that with respect to these components of the data set, the SOE monitoring does cover the flows that occur the majority of the time.

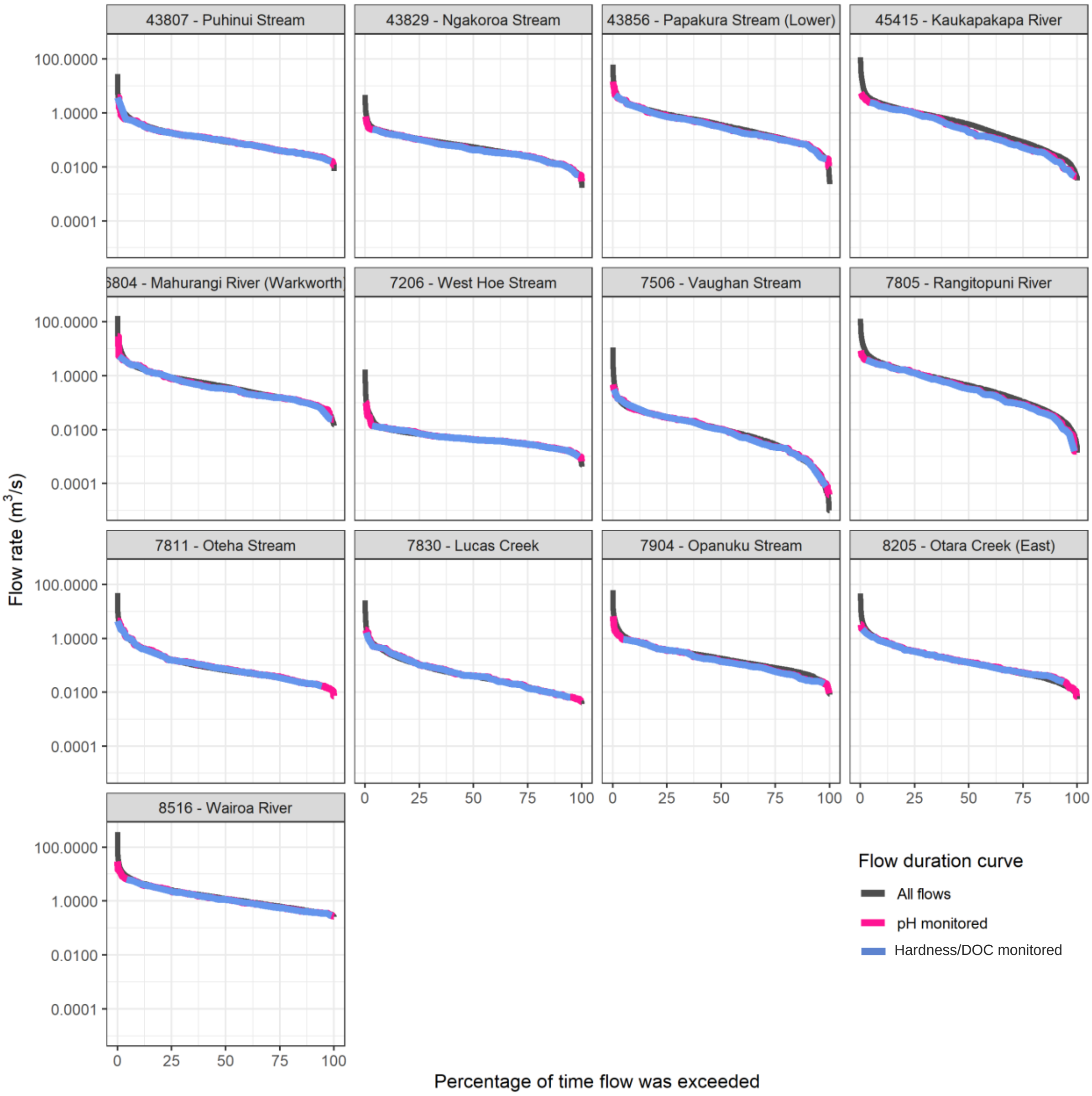

Figure 3-2: Comparison of flow duration curves from all available flow data (hourly averages, data up to June 2021) and flows measured during SOE water quality sampling (up to June 2021). Curves are drawn in the order from most extensive to least - grey (back), pink, blue (front). Note that water quality monitoring has typically not been undertaken at the highest flows and for some sites, at the lowest flows.

High frequency water temperature and flow data for Auckland streams were first viewed and then obtained from AC's Environmental Data Portal. Analyses of DOC during storm events were undertaken specifically for this project, using samples collected during a storm event at two sites in south-east Auckland – in the Wairoa River and the Aroaro Stream. Samples were collected at these sites using automatic samplers (ISCO 3700) connected to water level instruments to trigger sampling during storm events. Samples were analysed by NIWA's water quality laboratory in Hamilton for

Dissolved (Non-Purgeable) Organic Carbon using high temperature catalytic oxidation and IR detection after filtration (see APHA 5310B).

Additional water quality data (including pH data) for New Zealand rivers were obtained from NIWA's National River Water Quality Network (NRWQN) which includes rivers throughout New Zealand; supplemented with related studies on those same rivers (Scott et al. 2006, Smith & Maasdam 1994).

The data analysis in this chapter uses graphical techniques such as box plots, scatter plots, and descriptive statistics to characterise data and identify patterns. As stated in the introduction to this chapter, data analyses presented are exploratory only, with minimal use of statistical analyses or tests to compare between groups/factors. This approach was used because the primary data set (SOE data) is not well-balanced in terms of the number of sites within each categorical grouping (land cover / watershed) and there is potential to find statistically significant but misleading results. All analyses were carried out in R (R Core Team 2020) and used the Tidyverse (Wickham et al. 2019) library for the data wrangling. The graphics were also produced in R using cowplot (Wilke 2020), ggfortify (Tang. et al. 2016), ggplot2 (part of the Tidyverse), RColorBrewer (Neuwirth 2014), and scales (Wickham & Seidel 2020) libraries.

3.3 Water temperature

Like air temperature, river and stream temperatures show both diurnal and seasonal variation. Variation across the region can also be expected according to climate zones and land cover / land use; and between streams depending on the amount of shade present (due to vegetation or topography). Processes affecting water temperature in urban streams, where metals are more likely to reach concentrations of concern for aquatic life, are described in detail by Young et al. (2013). Briefly, water temperature can be increased by runoff from heated impervious surfaces conveyed by piped networks, and this can be exacerbated in catchments where baseflow is reduced due to urban development (Young et al. 2013). Furthermore, water temperature is influenced by flow though this can be a less significant factor (Young et al. 2013).

Analysis of monthly SOE data for a period of 5 years (2016-2020)[4] indicates Auckland rivers and streams show limited differences in temperature variation by watershed (acknowledging disproportionate representation of some watersheds, including lesser representation of North East, West Coast, Mahurangi, Hauraki Islands and Wairoa catchment receiving environments in SOE data). However, despite this variable coverage, there are apparent differences between individual stream sites, which appear to be influenced by catchment land cover (Figure 3-3). Median and interquartile ranges of water temperature are lower at sites with predominant native or exotic forest cover, and higher at the sites dominated by urban land cover.

Water temperature demonstrates clear seasonal variation at all sites (Figure 3-4), and although at some sites there appears to be a loose relationship between flow and water temperature in the SOE data (Figure 3-5), this is confounded by higher flows occurring in winter, and lower flows occurring in summer. There is also considerable variation in the relationships, indicating factors other than flow influence water temperature. Note also that the range of flows covered during SOE monitoring is somewhat limited, as this sampling is biased toward grab sample collection during baseflow conditions (see section 3.2 and also Montgomery et al. (2022)).

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[4] The full SOE data set was restricted to the time period January 2016 to December 2020 to ensure full calendar years included and to ensure comparability between sites given climatic variation over time.

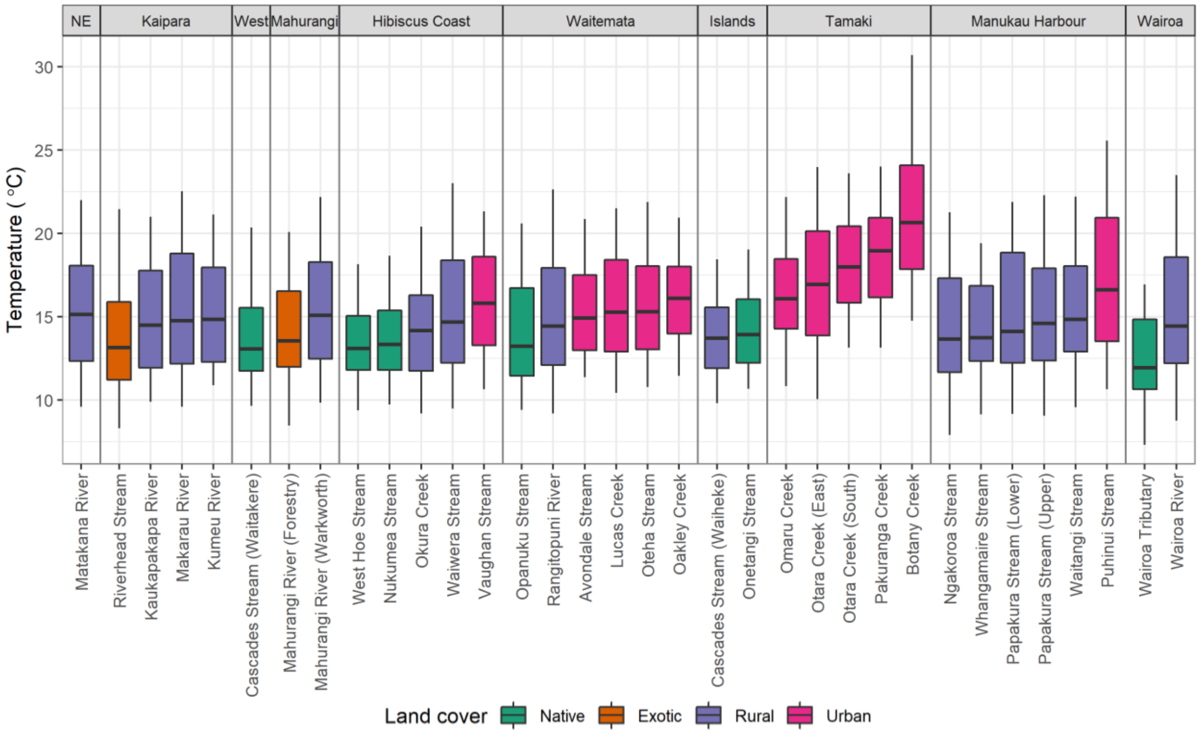

Figure 3-3: Comparison of monthly SOE sampled water temperature between individual stream sites and between watersheds. Data from January 2016 to December 2020. Five years of data used to ensure full years of data and for comparability between sites. Box spans inter-quartile range, horizontal line represents median and whiskers extend to observed value closest to 1.5 x interquartile range. NE = North East, West = West Coast. Within each watershed, streams are ordered by median temperature and coloured by land cover category.

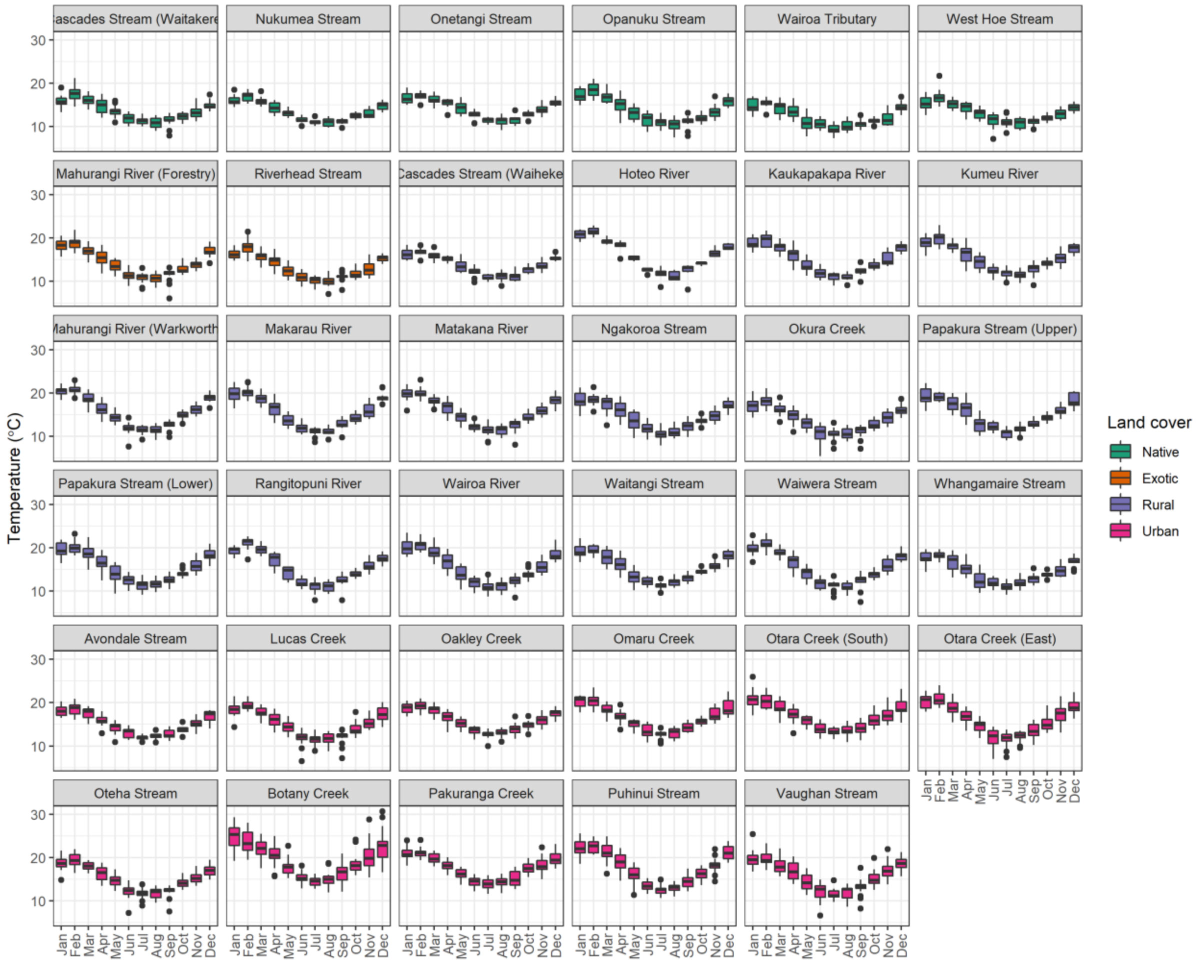

Figure 3-4: Seasonal variation in monthly sampled SOE water temperature within individual stream sites. Data from January 2016 to December 2020. Five years of data used to ensure full years of data and for comparability between sites. Box and whisker plot statistics as per Figure 3-2.

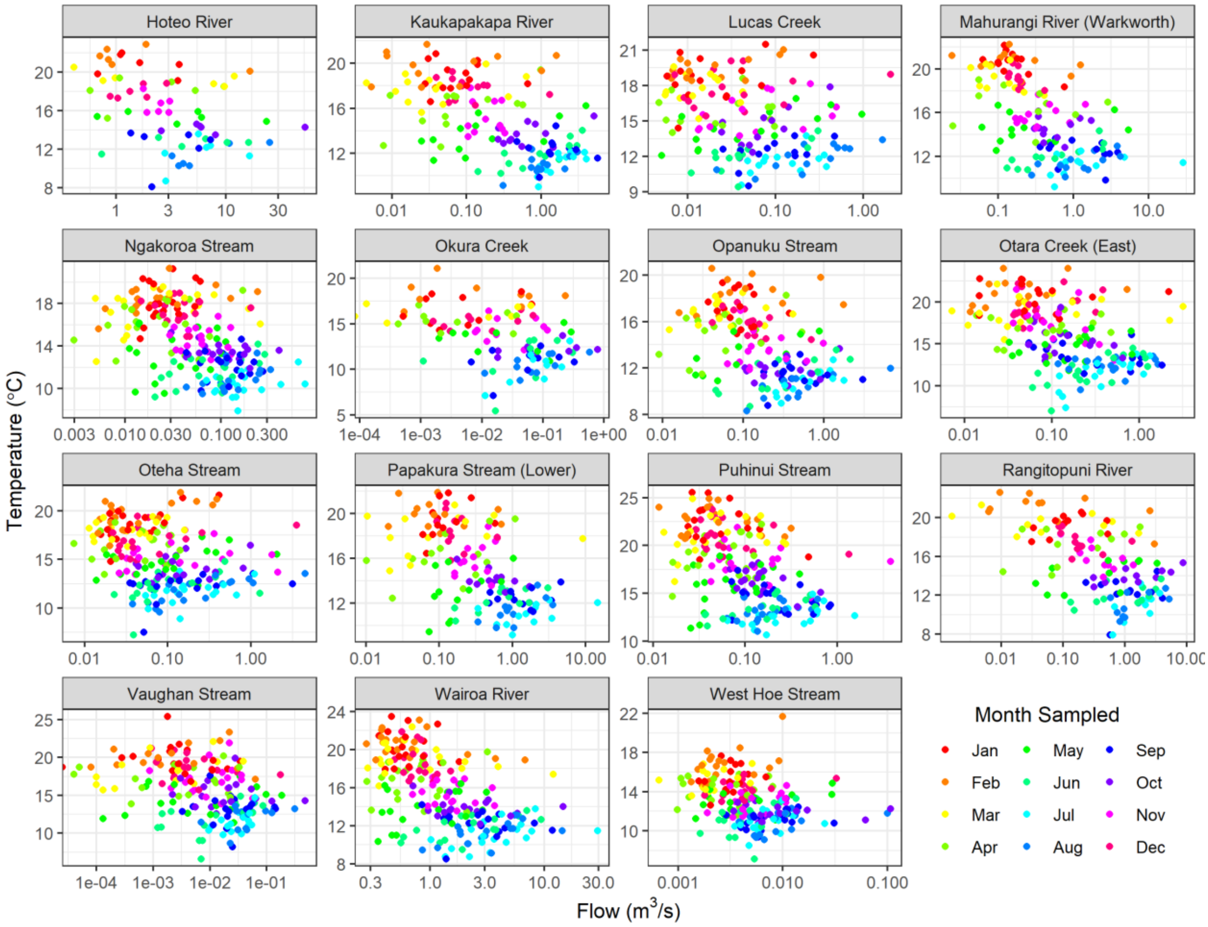

Figure 3-5: Relationships between monthly observed SOE water temperature and stream flow within individual stream sites. Data from January 2003 to June 2021. All available data used in this assessment to provide maximum number of data points at each site. Note x-axes (flow) and y-axes (temperature) are different on each plot.

When the influence of flow on water temperature is examined on a finer temporal scale (e.g., from 15-minute data, see Figure 3-6), stream flow can influence the temperature, and the diurnal variation in temperature. In summer, higher flows may be associated with higher temperatures, probably related to runoff from hot surfaces whereas in winter the reverse can occur. At any time of year, the change in flow typically disrupts the diurnal variation. Figure 3-6 shows, for example, how high flows at the Wairau Creek at Chartwell Road monitoring site disrupts the diurnal temperature cycle and tend to increase summer stream temperature (Figure 3-6a) but reduce winter stream temperatures (Figure 3-6b). This indicates there is some complexity in the influence of stream flow on water temperature – however seasonal variation is likely to remain the major influence, with observed differences of up to 10°C between summer and winter (based on SOE data, mainly at baseflow).

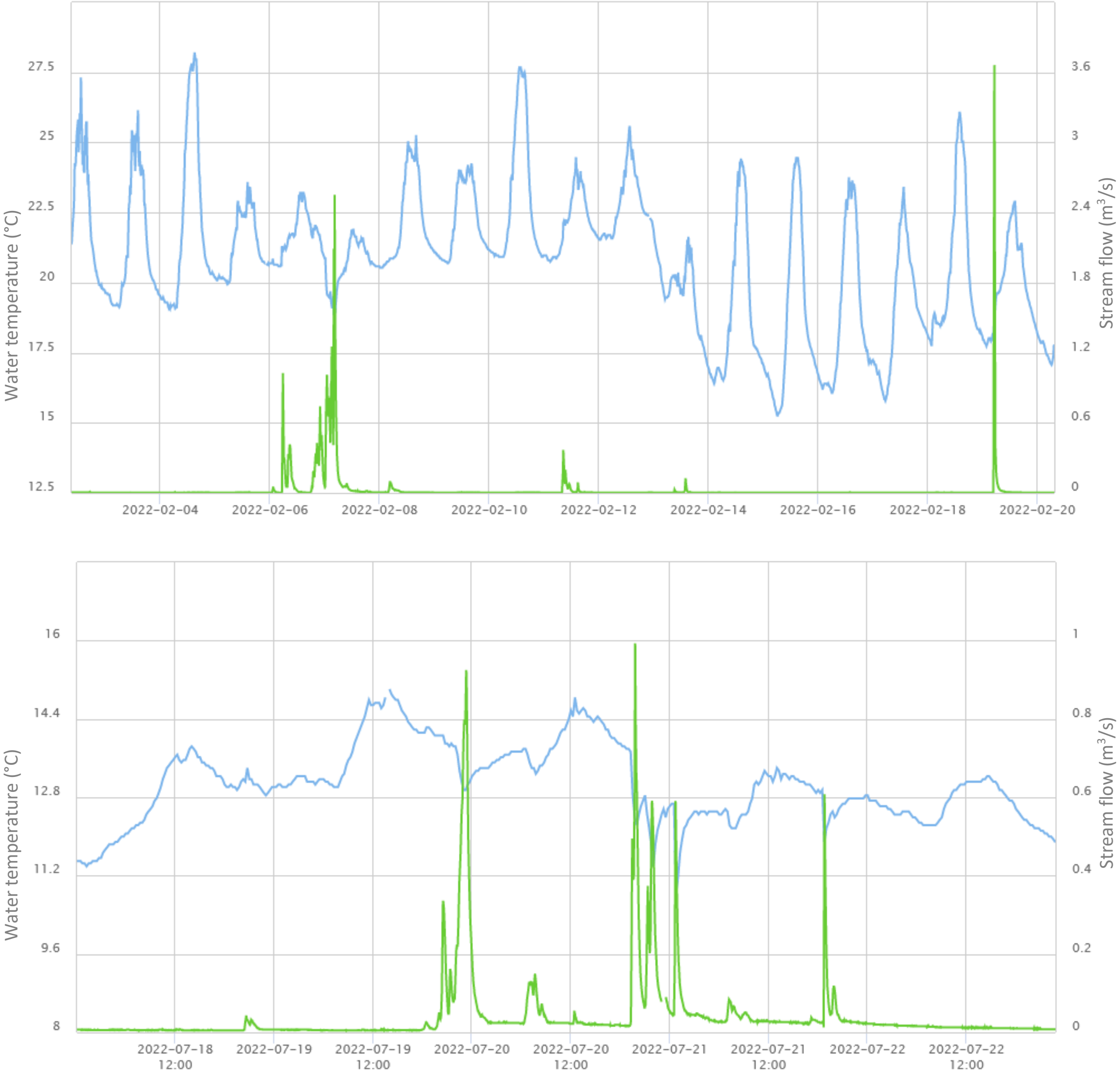

Figure 3-6: Influence of stream flow (green line) on water temperature (blue line) when measured at 15-minute intervals. In February (top plot) rainfall (and higher flow) results in higher temperatures; in July (bottom plot) rainfall reduces stream temperature. All data are for Wairau Creek at Chartwell Road, accessed via and plotted in Auckland Council Environmental Data Portal.

3.4 pH

The pH of most natural waters lies between 6 and 9 with a relatively narrow range for any given waterbody and is governed by the interactions of acids and bases within the waterbody. The acids and bases present are a function of local geology (e.g., weathering of rocks) and biological processes such as photosynthesis and respiration that influence the carbonate balance through removal and addition of CO_2 (Stumm & Morgan 1996). These two biological processes result in diurnal variation in pH (Figure 3-7): photosynthesis decreases CO_2 and H^+ ions (through formation of carbonic acid), thus increasing pH; while respiration increases CO_2, increasing H^+ ions and decreasing pH. This variation is strongest in streams with high levels of aquatic vegetation (algae / periphyton / macrophytes) and in streams with low alkalinity, where buffering is lower (Davies-Colley & Wilcock 2004). Photosynthesis and respiration can also result in seasonal variation. Higher pH generally occurs in summer months when aquatic plants are more abundant and sunlight hours are longer; exacerbated by lower water levels during summer. This seasonal variation is apparent at a few Auckland sites such as Botany Creek, Nukumea Stream and Riverhead Stream, with a difference of 0.5 - 1 pH unit between months with the highest and lowest pH, but the variation is either very minor or not apparent at the majority of sites (Figure 3-8). This means that seasonal variation may not need to be considered if using pH to adjust zinc water quality guideline values.

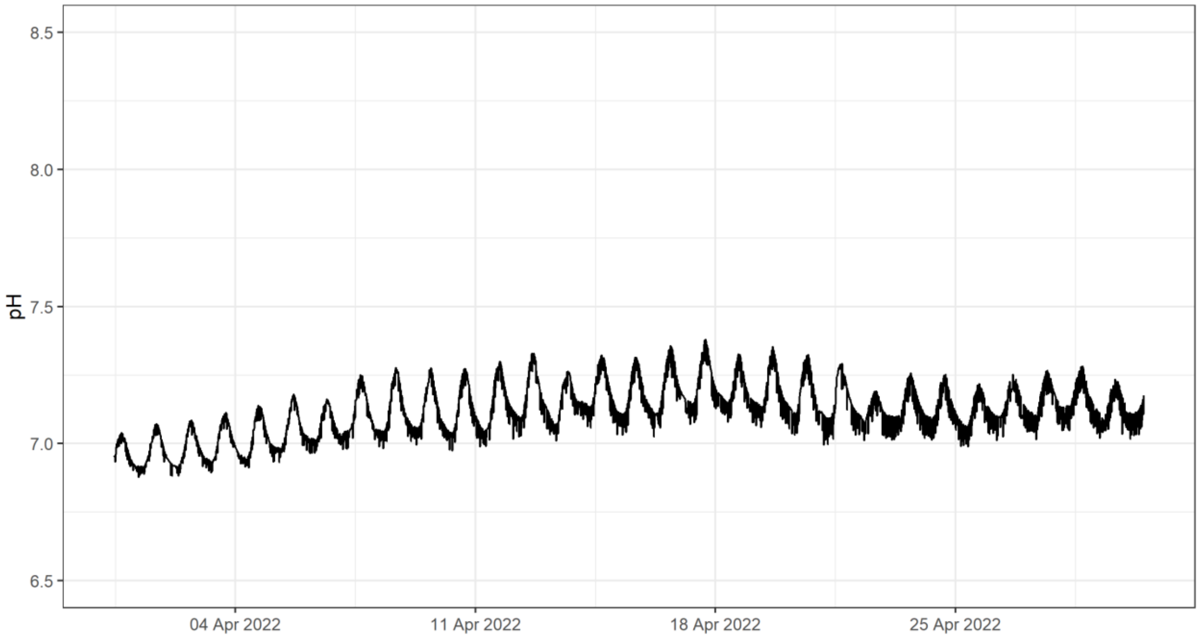

Figure 3-7: Diurnal variation in pH in Wairoa River at Tourist Road. NIWA unpublished data, as measured with YSI exo sonde, supplied by R. Davies-Colley. Larger diurnal fluctuations can be observed at sites with more primary production.

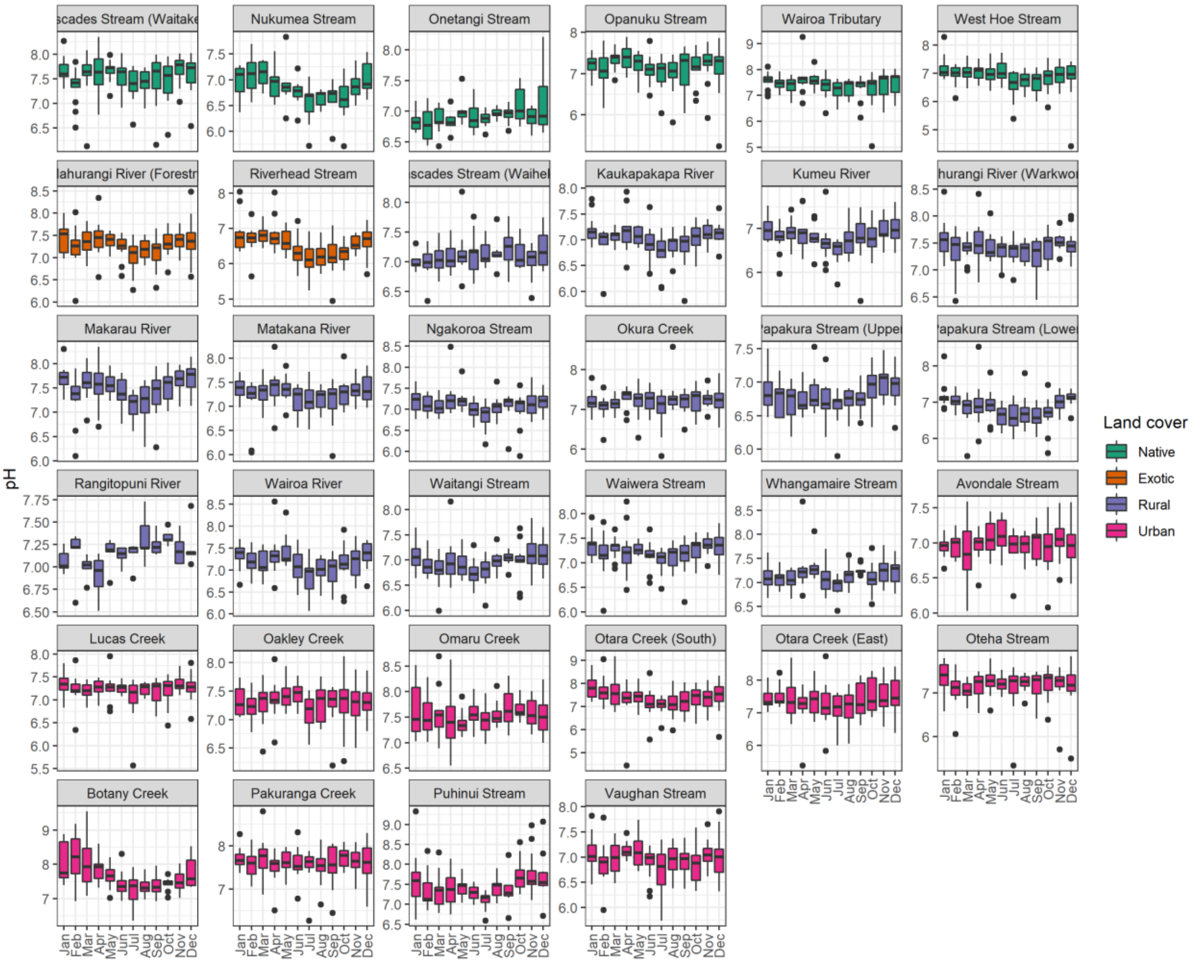

Figure 3-8: Seasonal variation in monthly observed SOE pH within individual stream sites. Data from January 2016 to December 2020. Five years of data used to ensure full years of data and for comparability between sites.

Other processes can also cause seasonal variation – for example in summer when water levels are low, the dissolved solutes present in the streams are more concentrated, which can either raise pH in the case of carbonates, or decrease pH in the case of humic acids. Furthermore, rain events can influence pH: rainwater has low pH (naturally ~5.6) due to the dissolution of carbon dioxide, which decreases the stream pH as it enters a stream, and therefore pH may be lower at times of high flow, typically in winter in Auckland. The potential influence of stream flow on pH is examined in Figure 3-9, based on SOE data for 14 rivers and streams. There does not appear to be a strong relationship between pH and flow for any of these stream sites, though there is some indication of lower pH at high flows in Kaukapakapa River and Papakura Stream. The absence of a clear relationship may be due to limited sampling at high flows in the SOE monitoring programme, or due to other (potentially interacting) factors.

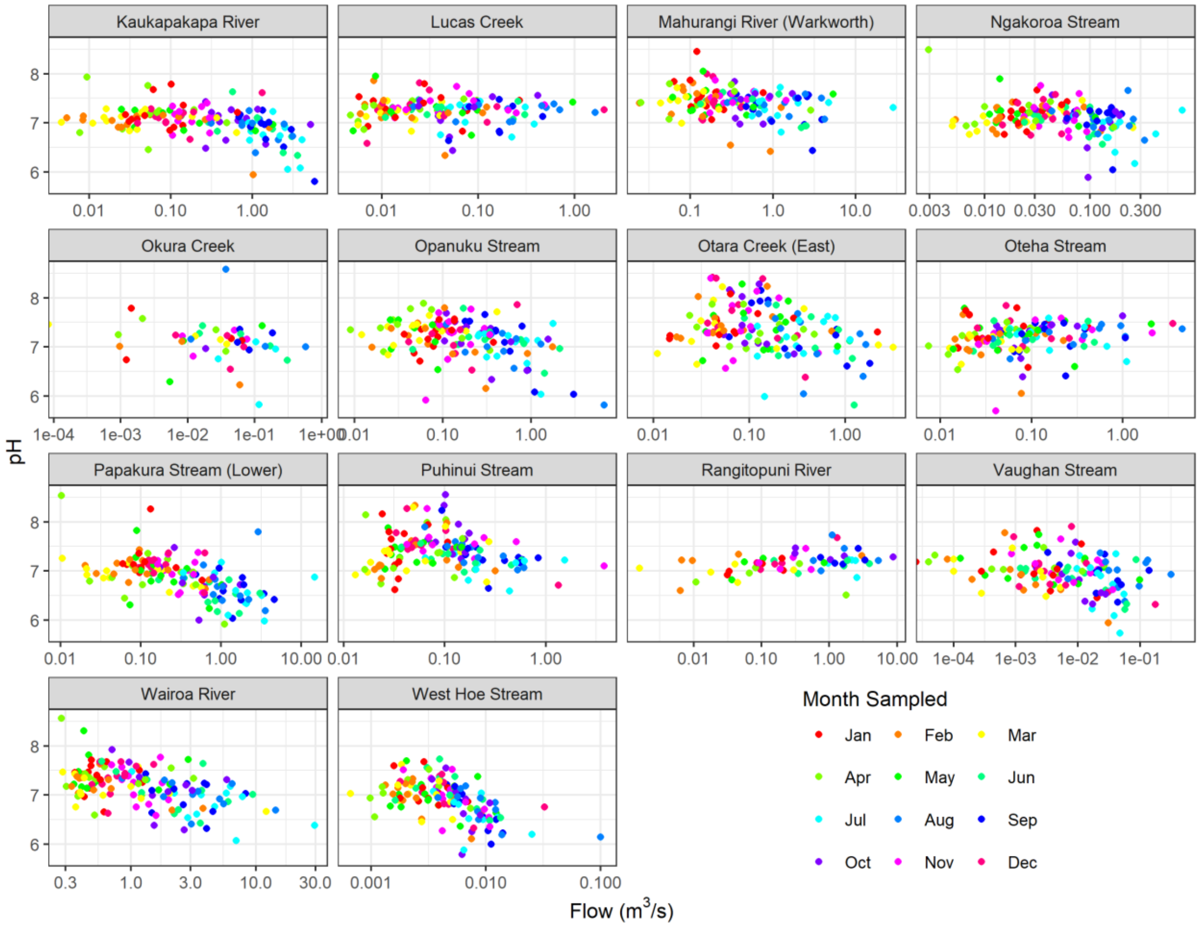

Figure 3-9: Relationships in monthly observed SOE water pH and stream flow within individual stream sites. Data from 2003 to June 2021. All available data used in this assessment to provide maximum number of data points at each site. Note x-axes (flow) are different on each plot. Several data points not shown as outside range of 5.7 to 8.6.

Geological and other catchment-based factors can also influence overall stream pH. In the majority of New Zealand rivers, the most important bases are bicarbonate and carbonates derived from carbonate rocks, and the buffering from bicarbonate means rivers and streams typically have pH between 7 and 8 (Figure 3-10, (Close & Davies-Colley 1990, Davies-Colley & Wilcock 2004)). Many of the streams monitored in Auckland have somewhat lower pH – between 6 and 7. This may be a reflection of the bias towards monitoring large rivers in the NRWQN, compared to the generally small rivers and streams monitored in Auckland. Stream pH outside the range of 7 to 8 does occur, depending on catchment geology and soils, amongst other factors. For example, in forested catchments, pH is typically higher where there is limestone geology, and lower in streams with high humic acids, such as lowland peat streams or West Coast forest streams (with natural accumulation of tannins leached from the bark of *Nothofagus* species). Streams affected by volcanic or geothermal activity can be highly acidic, due to the addition of hydrochloric acid and sulfur dioxide. Within urban areas, where metals are of most concern, pH can be affected by the amount of impervious surface, in particular concreted surfaces, which, as they weather increase stream alkalinity and thus pH (Kaushal et al. 2017). This process is discussed further in section 3.5, in relation to major cations and water hardness.

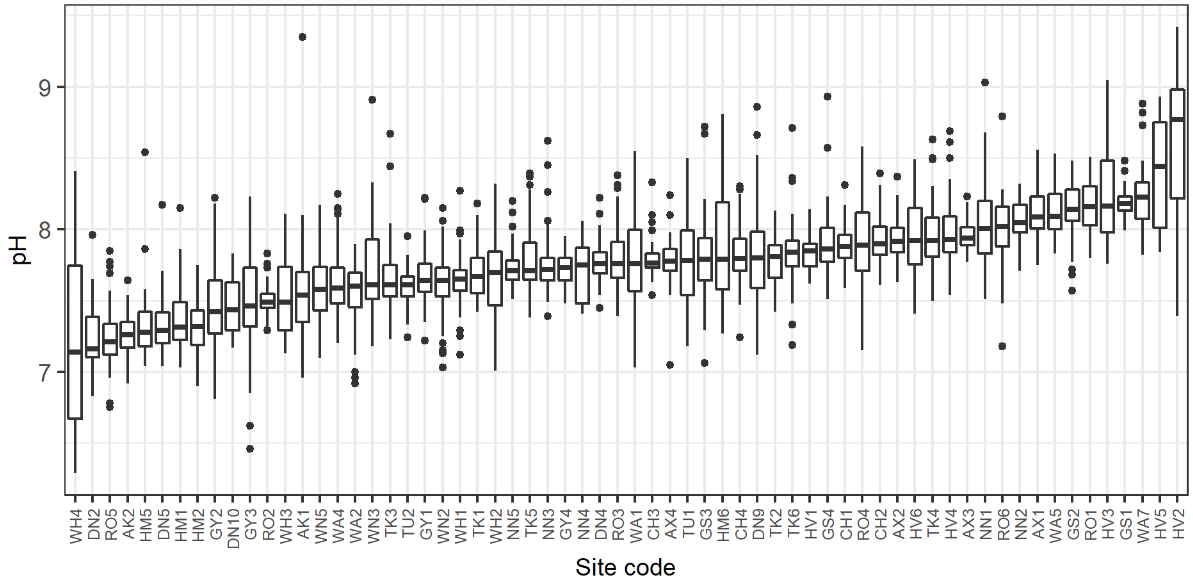

Figure 3-10: River pH from NIWA's NRWQN from 1989 to 2012.. Each box represents a specific site, sites are ordered from lowest median to highest median. pH data collected monthly, regardless of river flow. Site codes can be retrieved from https://hydrowebportal.niwa.co.nz/Data

Although there appear to be some differences in stream pH between the Auckland watersheds, which may reflect different geology and soils, this is likely confounded by the different number of streams monitored within each watershed, and differences in the land cover in those stream catchments (Figure 3-11). Streams in the Tamaki watershed are associated with higher pH, and urban land cover. Streams with exotic forest in the catchment can have lower pH than those with other land covers – a factor noted in previous studies of exotic forests in New Zealand (Collier et al. 1989). The higher pH associated with the Tamaki watershed and urban land cover could have implications for zinc toxicity, as toxicity to some aquatic organisms (e.g., algae) increases with pH (see section 2.3.3).

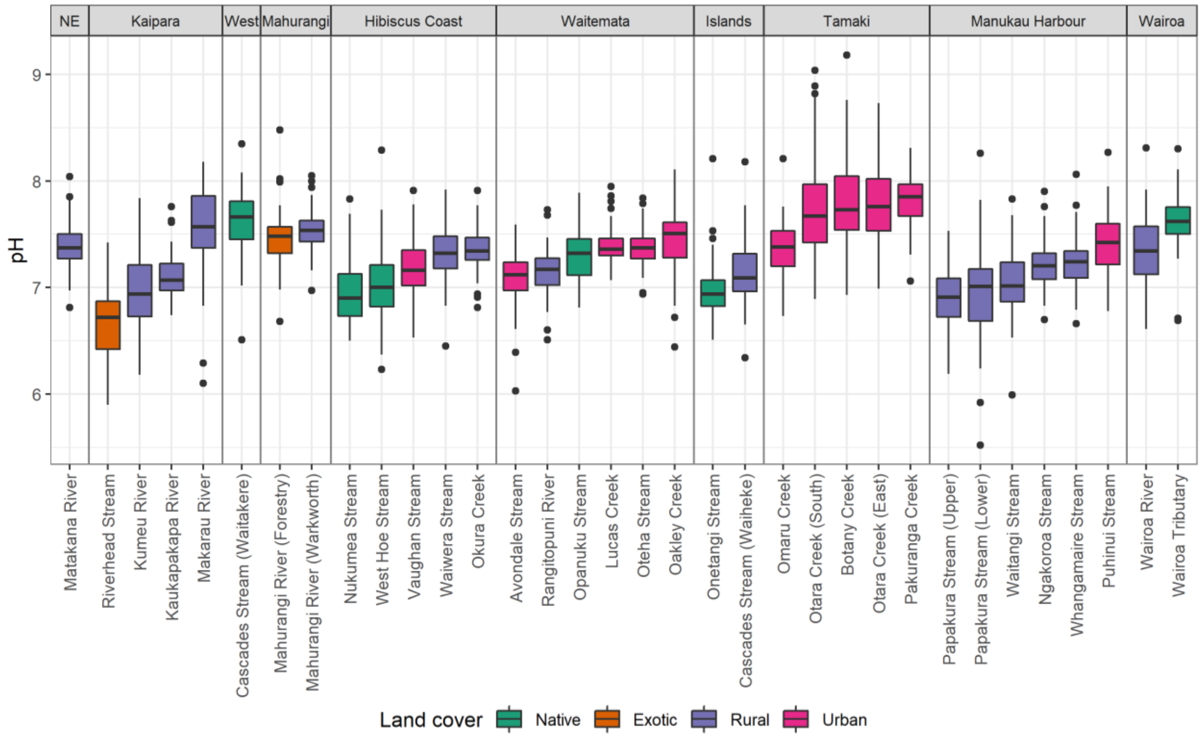

Figure 3-11: Comparison of pH in monthly observed SOE streams within Auckland watersheds. Data from January 2016 to December 2020. Five years of data used to ensure full years of data and for comparability between sites. NE = North East, West = West Coast. Boxes are coloured by land cover in the stream catchment.

3.5 Hardness

As mentioned above, the ionic composition of natural waters is influenced primarily by the weathering of rocks in the catchment and in any contributing groundwater and as such the chemistry (both composition and concentration) of freshwater streams can differs significantly between waterbodies. Major cations present are Na^+, K^+, Ca^{2+} and Mg^{2+} and major anions are Cl^-, SO_4^{2-}, HCO_3^-, $CO_3^{2-,}$ and in some cases NO_3^-. Calcium is the dominant cation in most streams, followed by sodium, magnesium and potassium. Sodium and chloride are more dominant in streams close to the coast, as coastal rainwater has a greater salinity and ionic proportions close to sea water. The concentrations of ions generally (but not always) increase from head-waters to sea, reflecting increased water residence time and concurrent increase in cations and anions from weathering (Tiwari et al. 2017).

As discussed in section 2.3, there are several major cations that influence metal toxicity of which the most important is calcium, followed by magnesium (depending on the metal and organism). There is fairly wide variation in concentrations of these cations in freshwaters across New Zealand, as reported by Close and Davies-Colley (1990) from baseflow sampling of 96 rivers, and by Smith and Maasdam (1994) from 12 months of sampling of 77 rivers. In the latter study, calcium concentrations ranged from 1.7 to 75 mg/L and magnesium from 0.34 to 10 mg/L (Figure 3-12). However, 75% of sites had median calcium less than 11 mg/L and magnesium less than 2.4 mg/L. Close and Davies-Colley (1990) reported that highest cation concentrations were measured at sites draining catchments dominated by soft sedimentary rocks as these yield more solutes than catchments with hard-rock geology (Drever 1982), and at sites with low rainfall, as high rainfall dilutes cation concentrations.

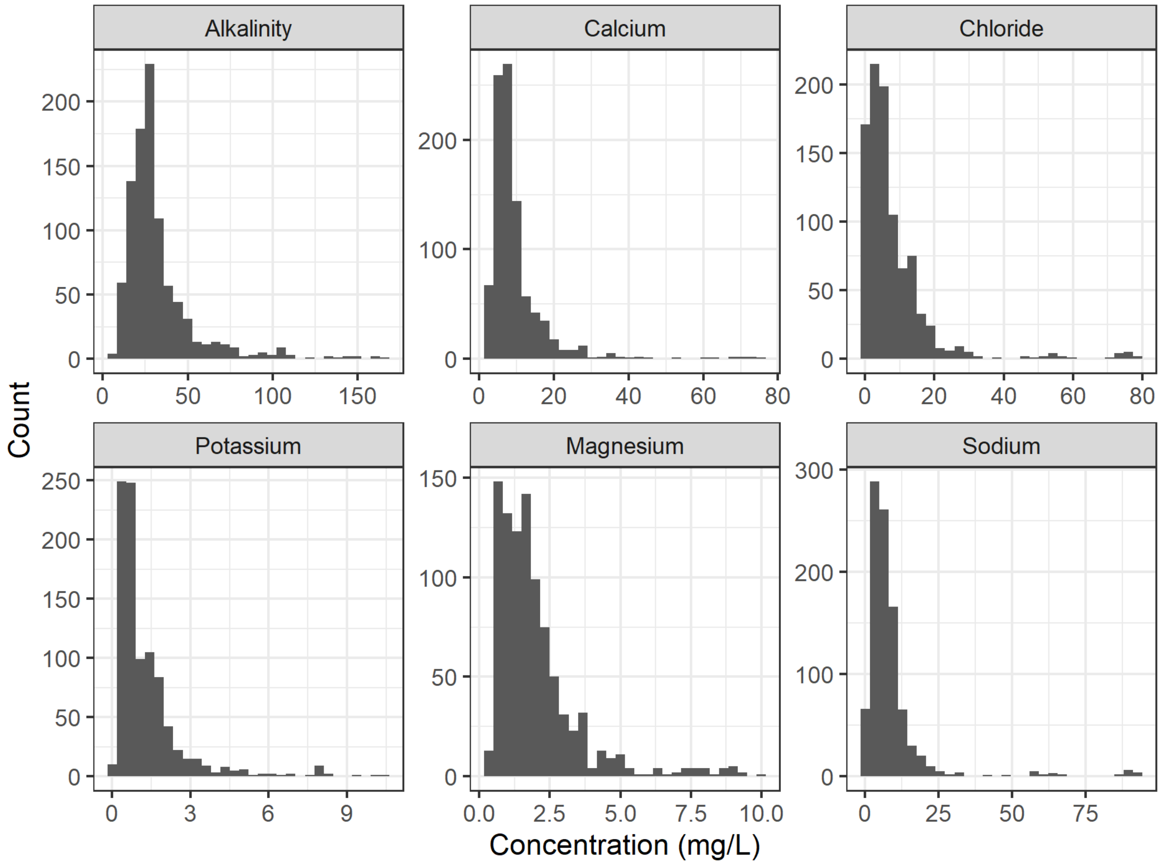

Figure 3-12: Major cations, chloride and alkalinity in New Zealand rivers. Data are from 12 months of sampling between January 1989 and May 1990, repeated in 77 rivers, from Smith and Maasdam (1994).

When comparing calcium and magnesium concentrations between the SOE sites in Auckland watersheds (Figure 3-13), there appear to be some regional differences. For example, the streams in Wairoa and West Coast watersheds have lower calcium and magnesium concentrations, and calcium appears to be highest in the Tamaki, Mahurangi and Waitemata streams. This is likely due to differences between watershed land cover of the monitored sites; for example, the SOE sites in the West Coast and Wairoa watersheds drain native and exotic forest catchments and all SOE sites in the Tamaki watershed drain urban catchments. High concentrations of calcium and magnesium in urban streams are consistent with findings in the US that these cations increase in concentration with increases in impervious surface cover, due to the weathering of concrete surfaces (Kaushal et al. 2017, Kaushal et al. 2014). Highest calcium, magnesium (Figure 3-13) and hardness (Figure 3-14) were measured in Pakuranga Stream – which not only has a high impervious surface cover in the catchment (46%, (Gadd et al. 2019a)), but the stream bed itself is concrete at the monitoring location (Figure 3-15). The calcium to magnesium ratio in urban streams of Auckland was consistently higher than the ratio in forested and rural streams (Figure 3-16), and more consistent between sites, suggesting a signature from concrete weathering. Note that this assessment is indicative only as the number of sites monitored differs between land cover types and is limited for native (n=6) and exotic forests (n=2). Statistical differences between the rural (n=15) and urban sites (n=11) are more reliable.

Relatively high concentrations of magnesium and, to a lesser extent, calcium at the Onetangi Stream site are likely related to the sampling location being very close to the coast and the rainfall here being enriched with salt water, as observed by the somewhat higher conductivity at this site (Ingley & Groom 2022).

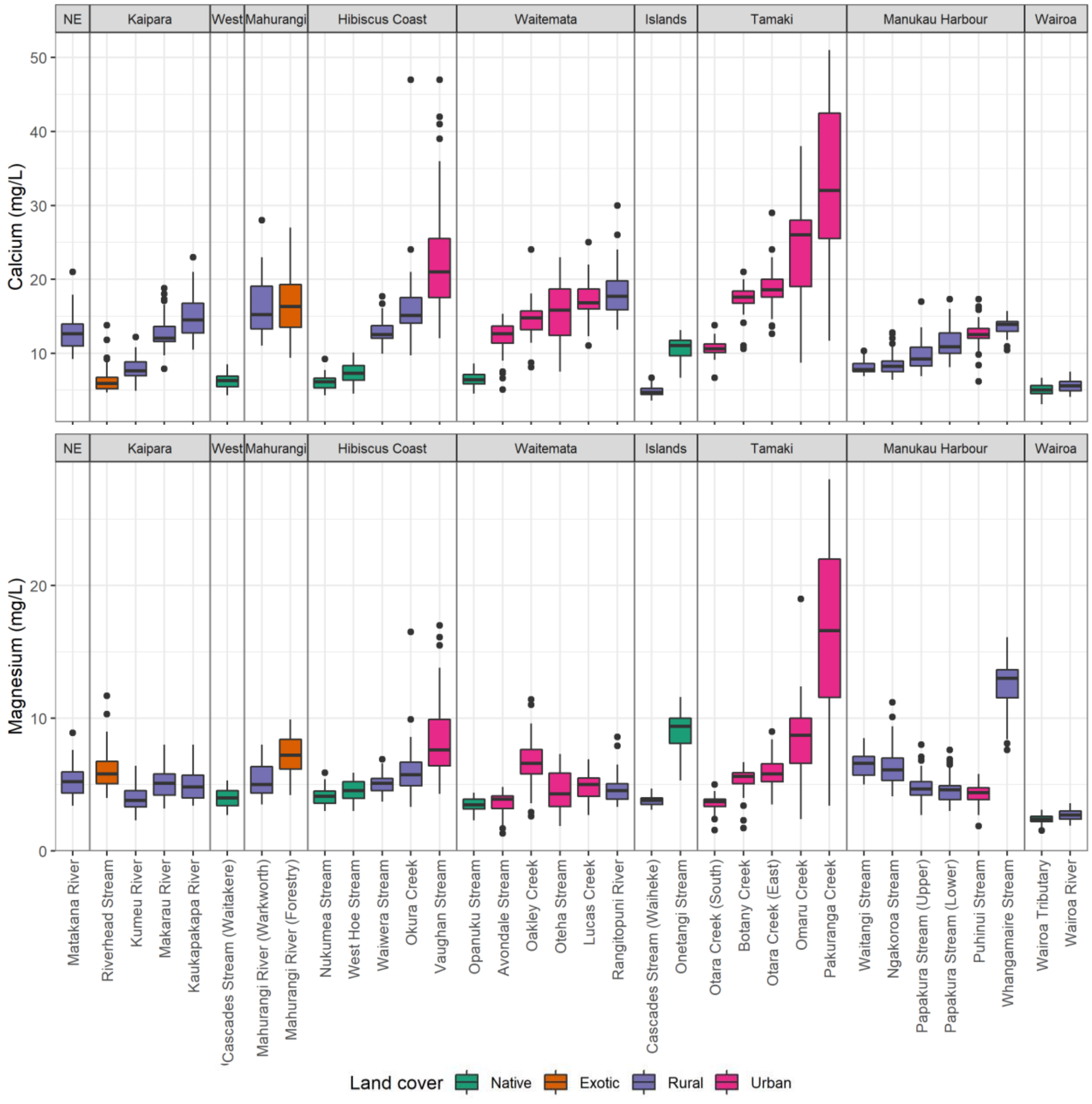

Figure 3-13: Comparison of calcium (top) and magnesium (bottom) in monthly observed SOE individual stream sites and watersheds. Data from November 2017 to June 2021. All available data used in this assessment to provide maximum number of data points at each site. NE = North East, West = West Coast. Within each watershed streams are ordered by median calcium concentration and coloured by land cover category.

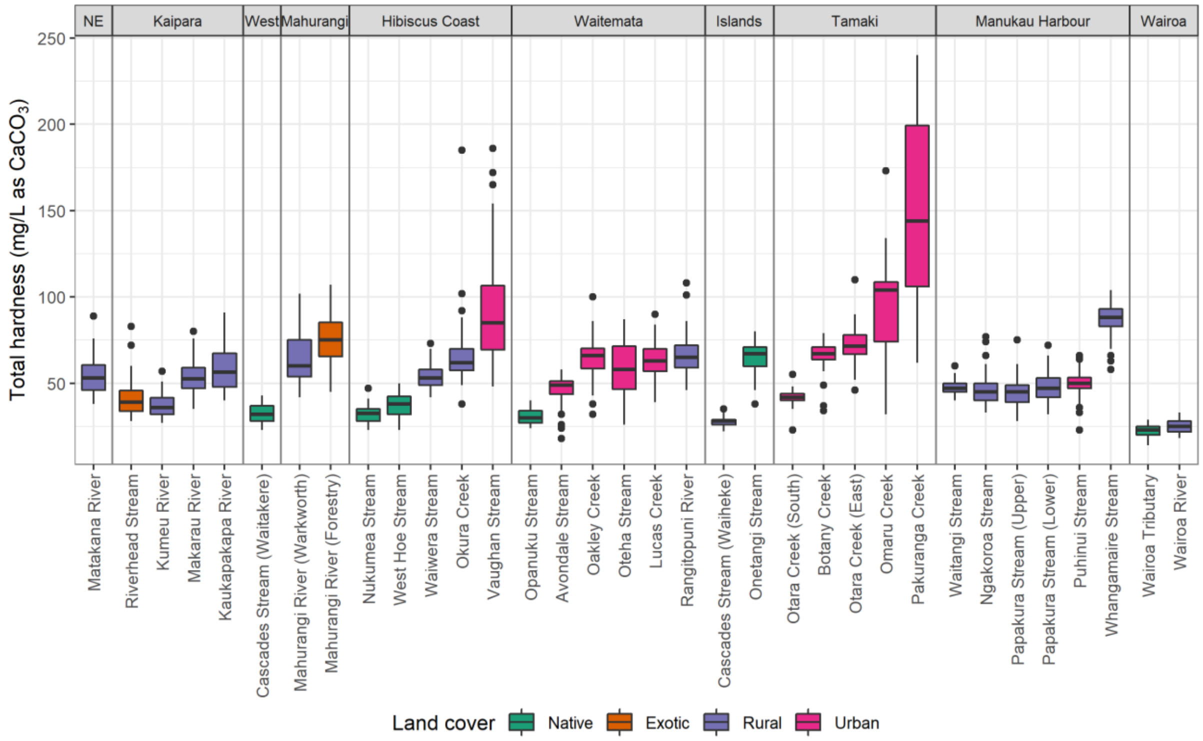

Figure 3-14: Comparison of total hardness in monthly observed SOE individual stream sites and watersheds. Data from November 2017 to June 2021. All available data used in this assessment to provide maximum number of data points at each site. NE = North East, West = West Coast. Within each watershed stream sites are ordered by median hardness and coloured by land cover category.

Figure 3-15: Location of water quality sampling in (left) Pakuranga Creek and (right) Otara Creek (south). Note concrete lined channel at Pakuranga Creek sampling location compared to natural stream bed in Otara Creek. Photos from lawa.org.nz.

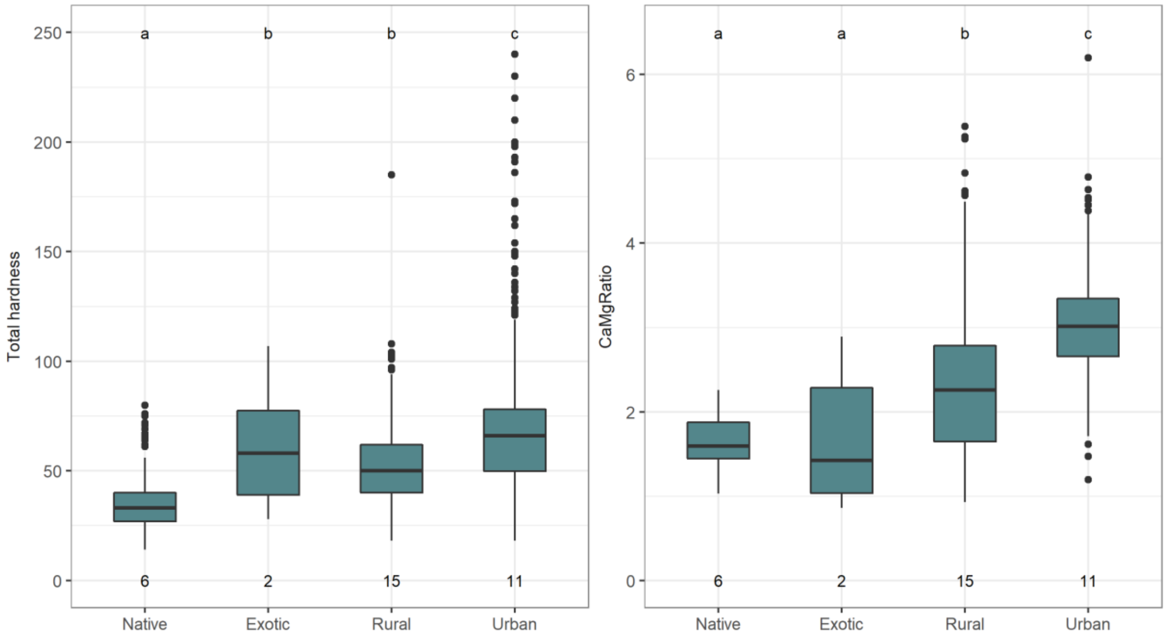

Figure 3-16: Comparison between land cover categories of total hardness and calcium to magnesium ratios measured in monthly SOE monitoring. Data from November 2017 to June 2021. All available data used in this assessment to provide maximum number of data points at each site. Letters at top of figure indicate statistical differences using pairwise Wilcoxon rank sum tests– groups with the same letter are not significantly different to each other. The number of monitored sites in each category is noted at the bottom of the plot.

In general, temporal variation in major cations and anions is largely related to flow. Dissolved solutes in the streams derived from weathered rocks and soils and groundwater inflows are at highest concentration during low flow (Davies-Colley & Wilcock 2004). At high flows, concentrations decrease as rainwater typically has lower dissolved solute concentrations, and this dilutes the calcium, magnesium and other cations and anions. For the Auckland streams where data are available, dilution at higher flows is observed for both calcium and magnesium concentrations at most stream sites (Figure 3-17). Note that the range of stream flows monitored does not cover the full extent of stream flows that occur at these sites (see section 3.2) but it does vary over at least one order of magnitude for all sites, and over two orders for most sites. This negative flow – concentration relationship results in a seasonal pattern at some Auckland stream sites (e.g., Vaughan Stream, Figure 3-18) though not at the majority of those monitored.

At some sites (including Rangitopuni River and Papakura Stream) the negative flow-hardness relationship is not as obvious or has more scatter (Figure 3-17). In some locations, solutes increase in concentration (at least briefly) as rainfall increases delivery of these solutes to the stream (Davies-Colley & Wilcock 2004). Anthropogenic processes also influence the cation concentrations such as soil disturbance from construction, forest harvesting or horticultural activities, which increase the availability of rock and soils for weathering and leaching of anions and cations (Likens et al. 1998). This may be the cause of the higher calcium concentrations in winter observed in the Rangitopuni River and Mahurangi River (forestry site), whereas other sites demonstrate highest concentrations in summer/autumn (Figure 3-18).

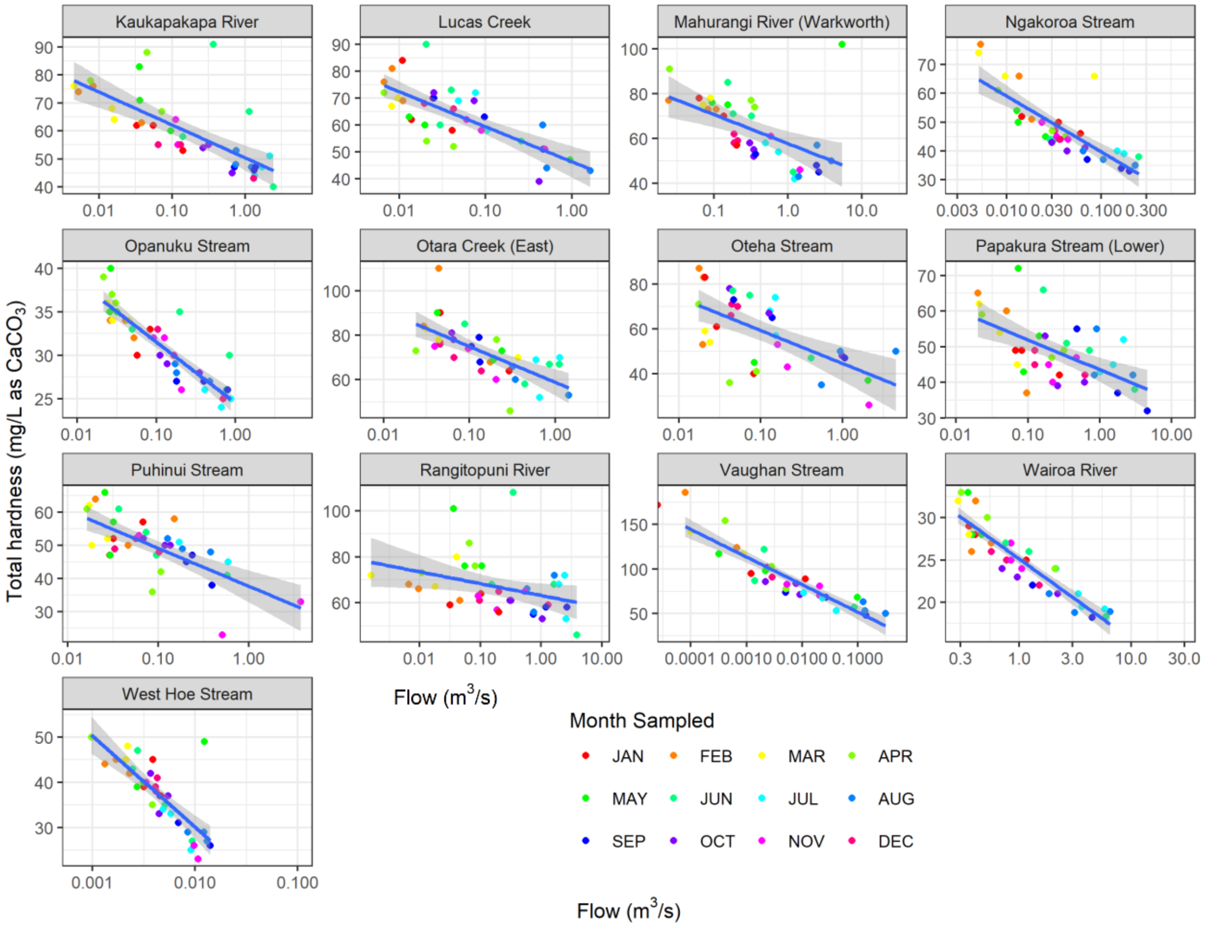

Figure 3-17: Total hardness concentrations versus stream flow, using monthly observed SOE data. Data from November 2017 to June 2021. All available data used in this assessment to provide maximum number of data points at each site. Note x-axes (flow) and y-axes (hardness) are different on each plot. Dots are coloured by the month sampled as an indication of season. Blue line indicates linear regression and grey shaded area indicates the 95% confidence interval around that regression.

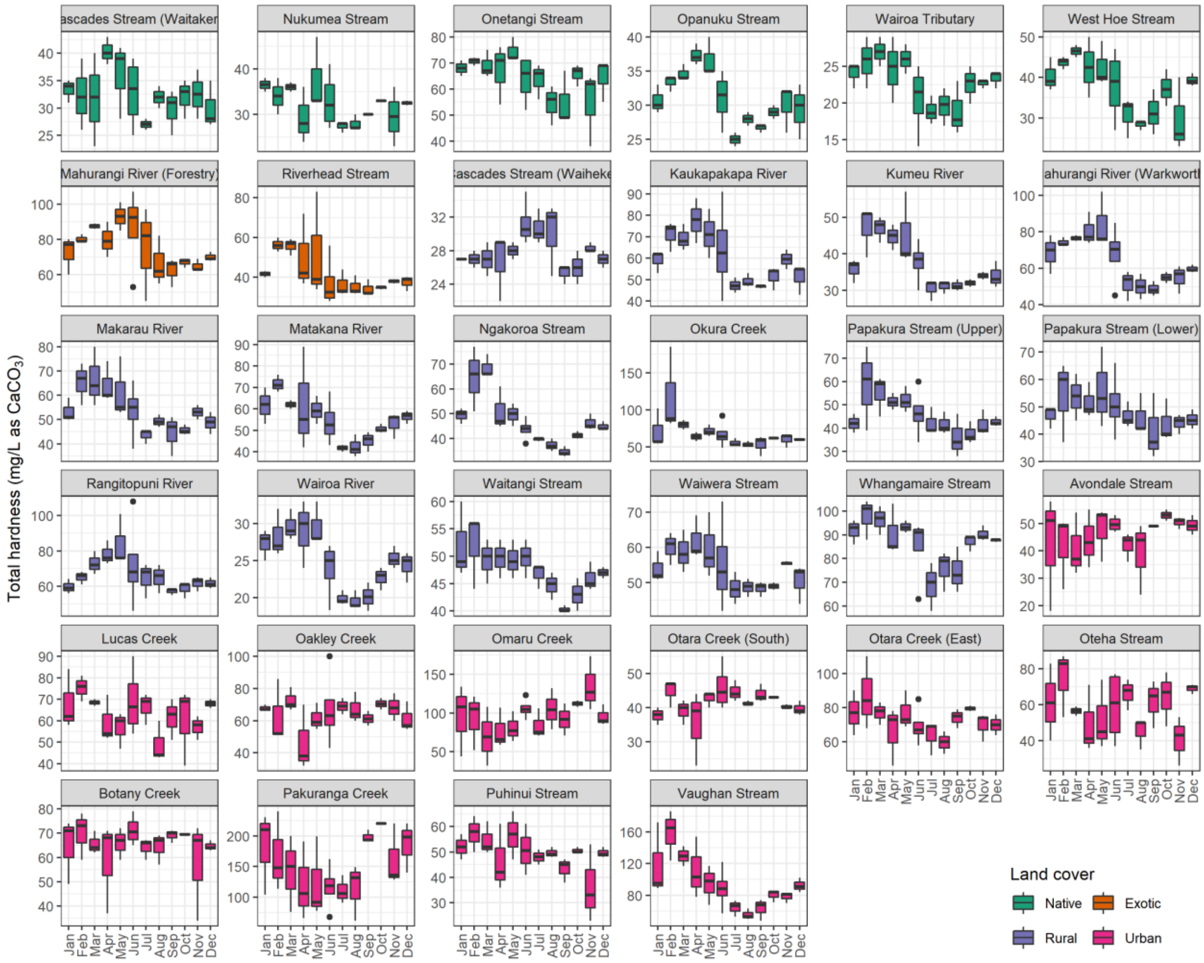

Figure 3-18: Seasonal variation in water hardness within individual stream sites monitored monthly (SOE data). Data from November 2017 to June 2021. All available data used in this assessment to provide maximum number of data points at each site. Note that this means the data are not evenly spread across seasons with slightly more data in summer-autumn.

3.6 DOM/DOC

DOM includes a broad range of different compounds from diverse sources, including those terrestrially-derived (allochthonous) and those microbially-derived within the waterbody (autochthonous). Of the terrestrial sources, the primary source (Ledesma et al. 2018) has been shown to be plant material dropping directly into a stream, from which organic compounds leach as the material degrades. In addition, plant material degrades on land, e.g., in leaf litter and soils, releasing compounds such as fulvic and humic acids which are transported into a stream via surface or subsurface flows (Pisani et al. 2020, Werner et al. 2019) This DOM source can be more important in flat catchments with high soil:water interaction, including areas with wetlands. Anthropogenic processes also contribute DOM, including wastewater discharges.

DOM includes a wide range of compounds, most of which are not identifiable, but also carbohydrates, carboxylic acids, amino acids, lipids and lignin (Lloyd et al. 2022). Some of these compounds rapidly degrade and others are stable – consequently no two waterways contain identical DOM concentrations and characteristics as the composition differs according to source.

DOM concentration (and composition) also changes with stream flow (Pisani et al. 2020), although the relationship between flow and concentration may not be consistent between sites and seasons (Werner et al. 2019). During stormflows, DOM concentrations can be higher than between events, and dominated by recently produced DOM (Pisani et al. 2020). However, this may not occur in cold climates/seasons where DOM mobilisation is lower (Werner et al. 2019). Alternatively, DOM can be higher during low flows, as water becomes more concentrated in DOC from degradation of terrestrial material or from autochthonous sources (i.e., generated within the stream).

Within New Zealand rivers, DOC (as a measurement of DOM) varies somewhat between sites (Figure 3-19) but also between samples (based on monthly measurements for 6-10 months, (Scott et al. 2006)). Over 90% of the rivers had median DOC concentrations less than 5 mg/L (median across all sites 1.9 mg/L). However, this data set includes only large rivers and does not include any lowland streams (which may drain peat areas) or West Coast streams, so this does not represent the true variation across New Zealand. For example, much higher DOC concentrations have been reported for several streams draining peat areas in both Waikato (e.g., 81-130 mg/L; Moore and Clarkson (2007)) and Southland regions (e.g., 20-30 mg/L; Physiographics of Southland (2016)), demonstrating that much higher concentrations are present in some locations. Furthermore, many South Island West Coast streams are characterised by their tannin-stained brown water, due to the high loads of organic matter from beech trees in the catchment and riparian zone.

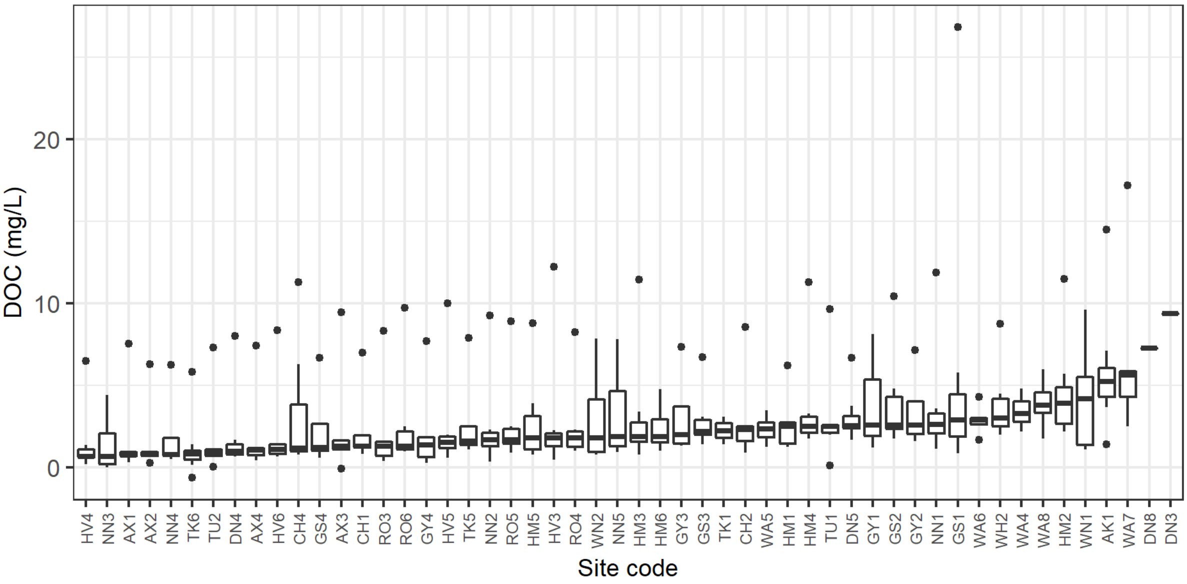

Figure 3-19: DOC concentrations in New Zealand rivers from the Scott et al (2006) survey. Each box represents a specific site, sites are ordered from lowest median to highest median. Data collected monthly, regardless of river flow for 6-10 months. Site codes can be retrieved from https://hydrowebportal.niwa.co.nz/Data

Based on the SOE monitoring at sites in the Auckland region, there are clear differences between streams, with median DOC concentrations ranging from 1.1 to 7.2 mg/L (data from November 2017 to June 2021) (Figure 3-20). There appear to be some links between catchment land use and DOC concentration, with lower DOC in streams draining native forest catchments (median concentrations ≤2.5 mg/L). Although there are some statistically significant differences in the DOC between land uses (based on analysis of variance and post-hoc tests with Tukeys ($p > 0.05$)), the observed differences may be due as much to the nature of these streams as the land use – the majority of streams with native forest in the catchment are second order, high gradient streams, where there is less opportunity for interaction between the plant matter/soils and the stream. By contrast, most of the streams in the rural category are on lowland plains. Rangitopuni River, with the highest median DOC (7.2 mg/L) is a 5th order meandering river in a low gradient valley. The median DOC in most urban streams was between 2.5 and 4.9 mg/L, with a slightly higher median in Vaughan Stream (6.1 mg/L). There are only two sites with high proportions of exotic forestry in the catchment and these showed very different DOC concentrations – ranging from a median of 2.7 mg/L in Mahurangi River to 6.2 mg/L in Riverhead Stream.

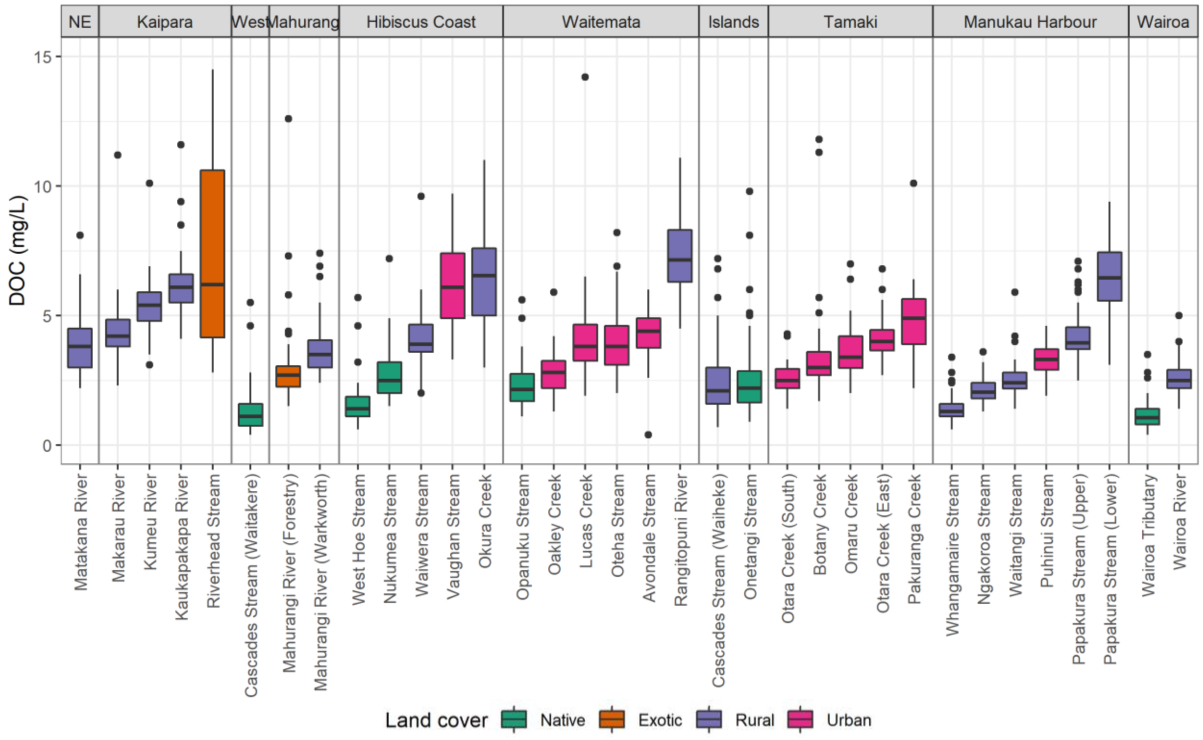

Figure 3-20: Comparison of DOC between streams based on monthly SOE Sampling. Data from November 2017 to June 2021. All available data used in this assessment to provide maximum number of data points at each site. NE = North East, West = West Coast. Within each watershed, stream sites are ordered by median DOC and coloured by land cover category. Note that three values for Omaru Stream of 23, 33 and 41 mg/L are omitted for visual clarity of other data.

There are visible seasonal differences in the monthly SOE DOC concentrations at several stream sites (Figure 3-21) - Riverhead Stream site, Kumeu River, Waiwera Stream. At these sites, lowest concentrations were typically measured in winter – around July / August and sometimes September. This may be due to decreased microbial activity in winter and increased activity in summer which then increases the DOC released into streams. It is also possible that some of the seasonal variation is due to flow; that is the highest flows occur during winter and the lowest flows in summer, which could result in greater dilution in winter and reduced dilution in summer. Graphical analyses of flow and DOC do not suggest any relationship between the two for the sites where there are flow data available (Figure 3-22), however there is no flow data for the Riverhead Stream, Kumeu River or Waiwera Stream, which demonstrated the strongest seasonal patterns. Few other sites demonstrated seasonal variation in DOC – though this may be partly due to variability over time and a lack of data, with only 3-4 data points per month available to date.

There are minimal data available for DOC at higher temporal resolution, for example from multiple samples collected within a day or within a storm event. Samples collected from the Wairoa River (at Tourist Road) and nearby Aroaro Stream during a storm event in March 2022 were analysed for DOC to partly fill this gap. These data (Figure 3-23) suggest minimal change in DOC (less than a factor of two difference) with changes in flow at these two sites. However, it is likely that other sites could show a different picture – for example in South Island forested streams, DOC is higher on the rising limb than falling limb (Moore 1989). The DOC dynamics are likely related to the relative timing of and inputs from riparian and catchment sources (McGlynn & McDonnell 2003), meaning that different dynamics can be expected at different sites.

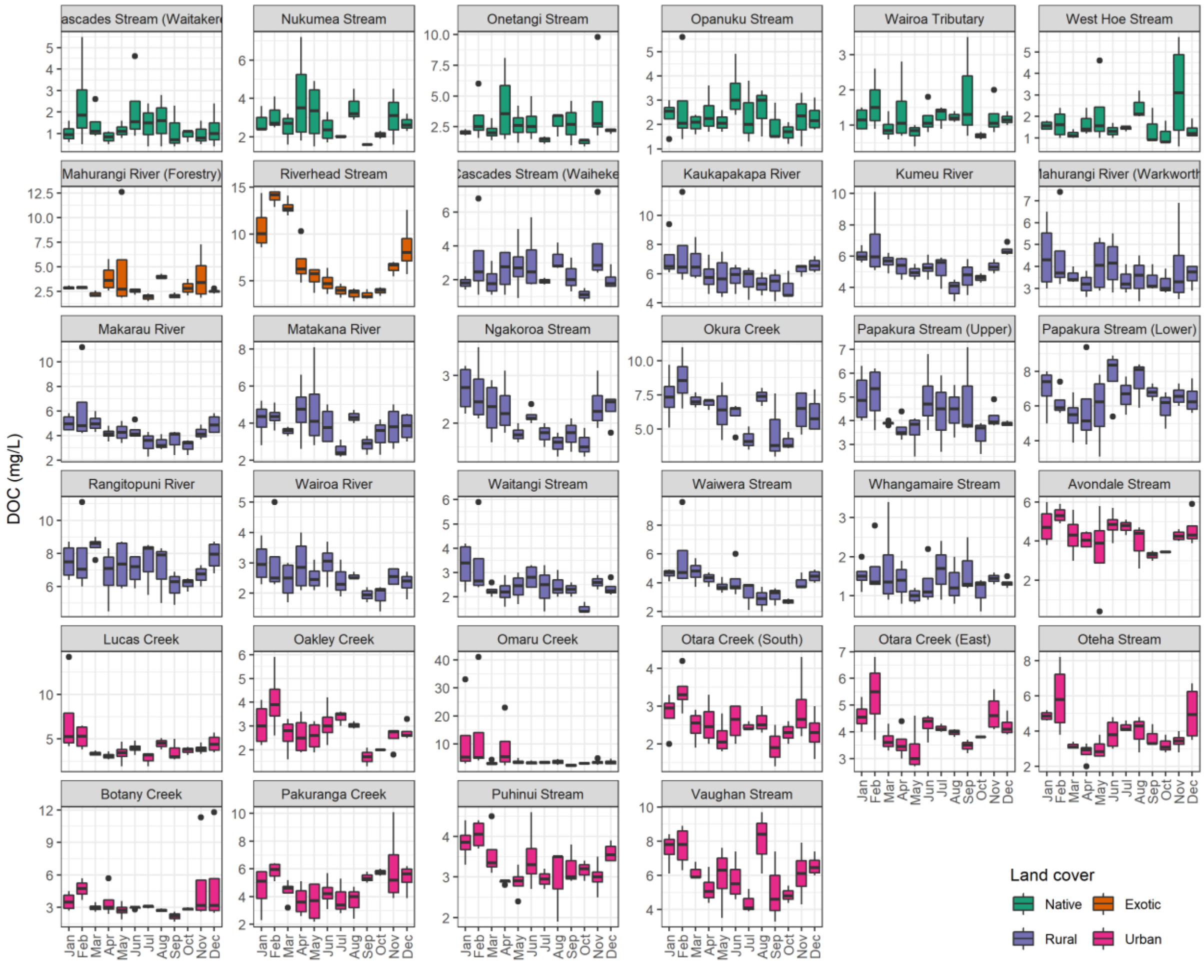

Figure 3-21: Monthly variation in DOC from SOE samples at each stream sampling site. Data from November 2017 to June 2021. All available data used in this assessment to provide maximum number of data points at each site. Note that this means the data are not evenly spread across seasons with slightly more data in summer-autumn. Note that y-axes vary on each plot. Box colour relates to the land cover in the upstream catchment.

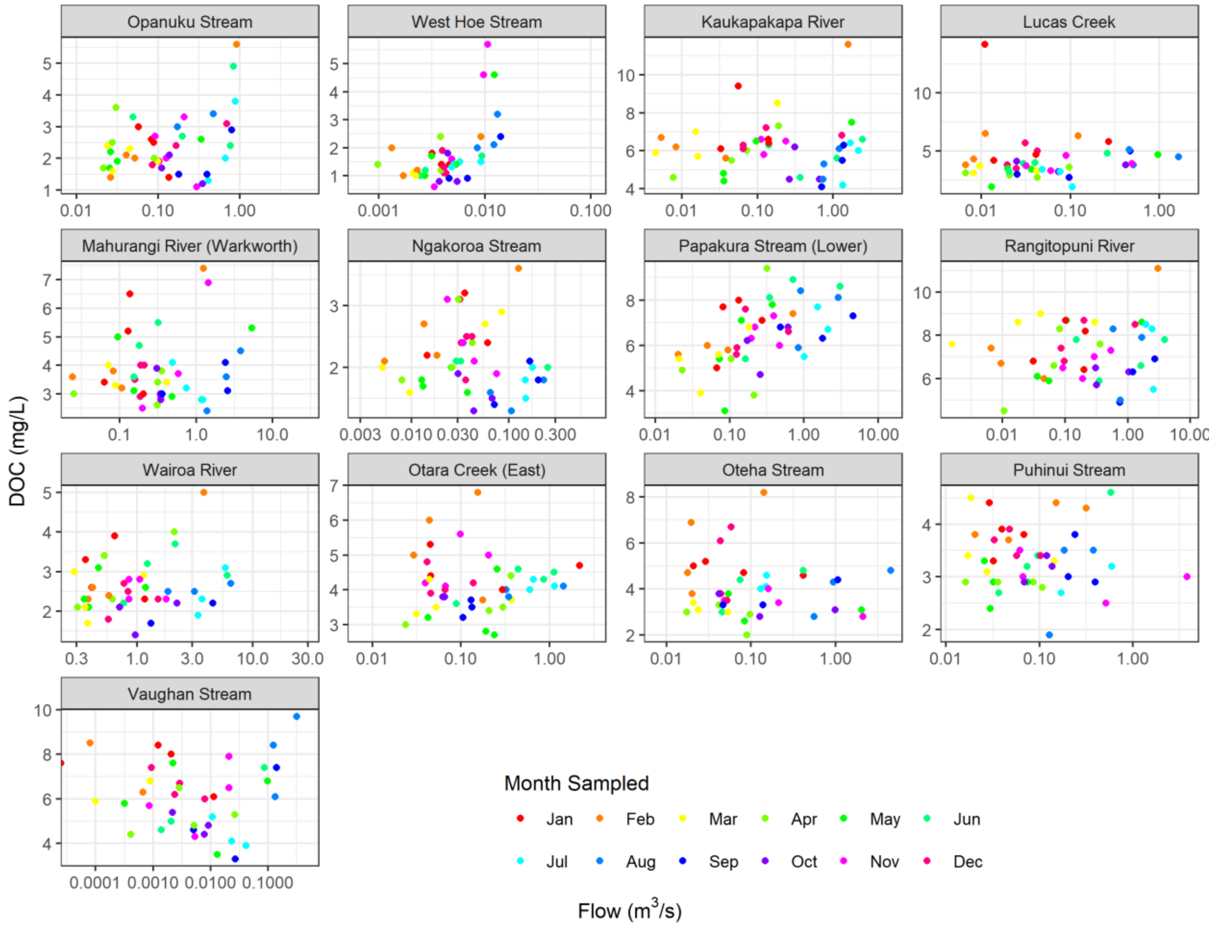

Figure 3-22: Relationships between DOC and stream flow from in monthly observed SOE within individual streams. Data from November 2017 to June 2021. All available data used in this assessment to provide maximum number of data points at each site. Note that the data are not evenly spread across seasons. Note both x and y-axes are different on each plot. Dots are coloured by the month sampled as an indication of season.

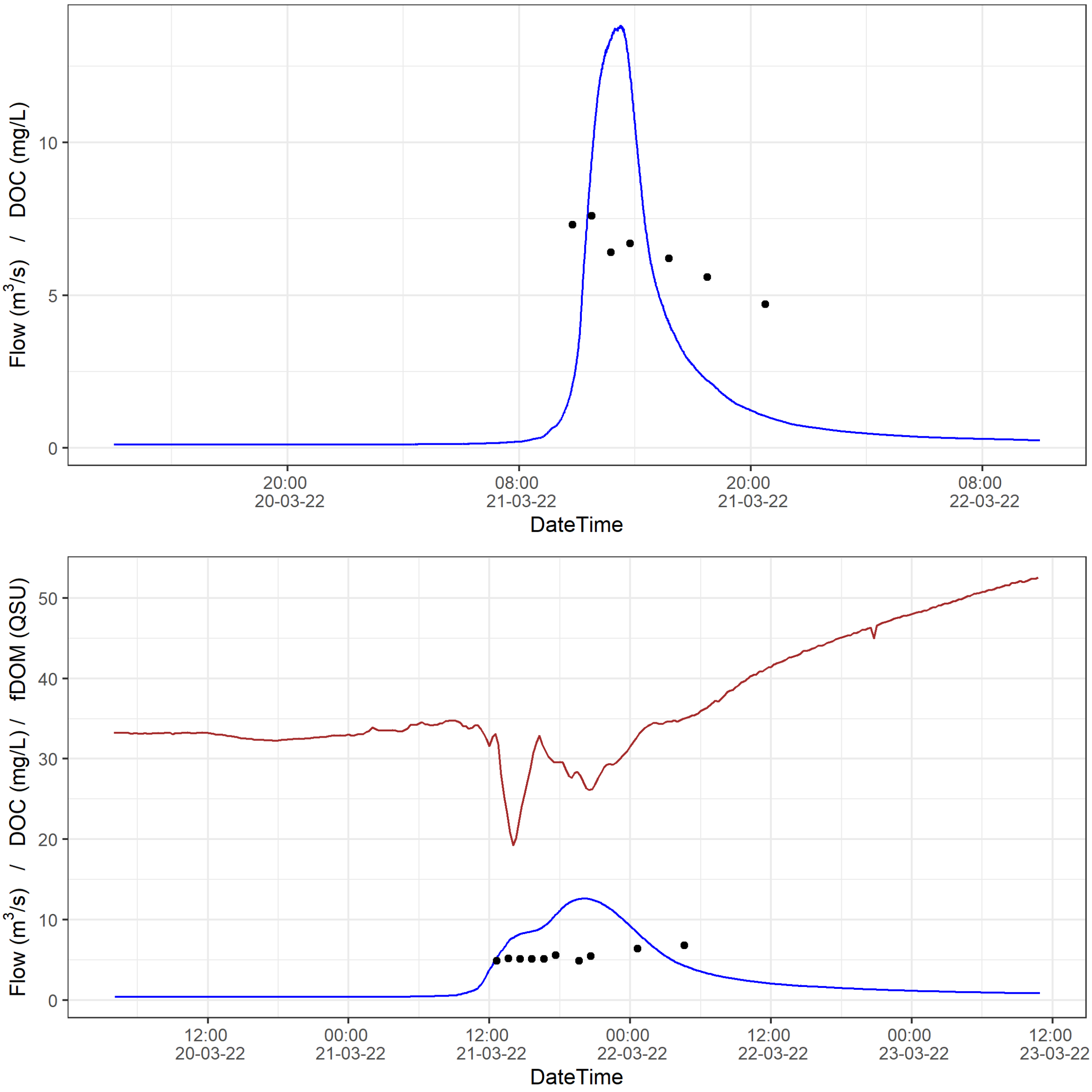

Figure 3-23: Changes in DOC during a storm event at two rural stream sampling sites: Wairoa River at Tourist Road (top) and Aroaro Stream at Ness Valley Road (bottom). Blue lines indicate stream flow, black dots indicate DOC concentration and brown line in bottom figure indicates fDOM measured *in situ*. Flow data for Wairoa River acquired from Auckland Council Environmental Data Portal. Sampling co-funded by NIWA SSIF programme.

3.7 Summary

The data available from Auckland's SOE monitoring network (and supported by additional data sets from Auckland and New Zealand) indicate that there were differences in the measured TMFs between the stream sites monitored, particularly for hardness and DOC. For example, median concentrations varied between Auckland SOE sites by a factor of 6.9 for magnesium, 6.8 for calcium, 6.8 for DOC, 6.3 for hardness, whereas median values varied by factors of only 1.6 for water temperature and 1.2 for pH.

Although the TMFs varied by site, there was no clear relationship between watershed (which may reflect geology and soils) and the values/concentrations of any of the four TMFs investigated (at least based on the data currently available, which is confounded by the issue of different land use in different watersheds).

Land cover did appear to influence concentrations of all TMFs (Table 3-3), but in different ways. Water temperature and DOC were generally lower in forested streams. Temperature, pH and hardness were highest at some urban sites. However, these relationships are not universal. Some urban streams have hardness concentrations lower than the overall median and some rural streams have hardness concentrations at the upper end.

All TMFs also varied temporally (both diurnally and seasonally), though this was arguably more important for temperature and to some extent DOC, than for pH or hardness. Indeed, the temperature range within any given site was greater than the differences between sites. Conversely, based on the data available (which does not reflect diurnal variation), the temporal differences in pH at a single site were relatively minor compared to the differences between sites.

All TMFs varied with changes in flow, however the extent (and direction) of that variation differed depending on the site, the TMF and the time of year. For temperature, changes in stream flow are expected to result in only minor and short-term spikes in water temperature. Similarly, minimal differences in pH occur due to changes in stream flow. On the other hand, calcium and magnesium concentrations (and the combined measure of total hardness) were clearly correlated to stream flow.

Table 3-3 below summarises the relationships between TMFs and the factors explored in this chapter – watershed, land cover, season and flow. The variation between sites and over time indicates that where TMFs are used to adjust metal guideline values, the best assessment of potential toxicity would be to use different values (particularly for DOC and hardness) for different streams / stream sites, and potentially at different flows (hardness only). Furthermore, if temperature is required for adjusting guideline values, seasonal variation should be considered.

Table 3-3: Summary of findings regarding relationships between TMFs and other factors..

TMF	Watershed	Land cover	Season	Flow
Water temperature	No clear differences	Higher temperature at some urban sites, lowest at forested sites	Strongly seasonal (lower in winter)	Weak relationship, confounded by season
pH	No clear differences	Higher pH at some urban sites	Weak/minor	Possible weak relationship some sites (lower pH at high flows)
Hardness	No clear differences	Generally higher hardness at urban sites	Seasonal variation at some sites, inconsistent pattern between sites	Lower hardness at higher flows
DOC	No clear differences	Generally lower at native forest sites	Seasonal variation at some sites (lower in winter), no clear variation other sites	No obvious relationship

4 Implications and recommendations for FWMT

4.1 Influence of TMFs on calculated water quality guideline values

The data reviewed in chapter 3 above indicate that there *are* differences in all TMFs between streams, with some TMFs varying by more than a factor of six between sites, and by more than a factor of two within a site over time. Whether such differences are important for water quality guidelines depends on the influence each TMF has on toxicity.

As some indication, in the freshwater copper guideline submitted as a draft for ANZG (2018), the copper guideline value approximately doubles as DOC doubles (Gadd 2021). Therefore, a difference in DOC from a low of 1.2 mg/L in the Wairoa tributary to a high of 7.4 mg/L in the Rangitopuni River (a factor of 6 difference), would be important in terms of changing (increasing) copper guideline values by around 6-fold; a substantially higher guideline value would be more appropriate for the Rangitopuni River. For copper, there is no recommended adjustment for varying calcium or magnesium concentrations or pH (Gadd 2021), so differences in these TMFs between sites will not affect guideline values.

For zinc, the effect of the different TMFs will depend on the bioavailability correction model(s) adopted for guideline derivation, which is still in development. However, as an indication, the Canadian long-term guideline value for zinc approximately doubles as hardness doubles, increases by a factor of 1.3 as DOC doubles, and decreases by a factor of 1.2-1.8 between pH 7.0 and 7.5 (depending on the values of hardness and DOC). This suggests that based on the differences observed between sites in these three variables, it would be appropriate to use different guideline values at different sites. For example, within the urban streams, the median hardness varies from 42 mg $CaCO_3$/L in Otara Creek to 144 mg $CaCO_3$/L in Pakuranga Creek – which could result in a >3-fold increase in the zinc guideline value between these locations[5]. On the other hand, differences in DOC and pH between urban stream sites (e.g., with median values that range from 2.5 to 6.1 mg/L and from 7.0 to 7.6 pH units respectively) could be expected to change the zinc guideline value somewhat less, by a factor of 1.4 to 1.6. As all TMFs may vary between sites, and have differing effects on the guideline values, the interaction of these may result in differences between guideline values that are greater or lesser than those stated here.

Given the extent to which DOC i) varies between sites (and to a lesser extent within a site), and ii) influences the copper guideline values, incorporation of DOC into numeric attribute states will be imperative when assessing the potential for copper toxicity in Auckland's streams. Similarly, given the likely influence of hardness on zinc guideline values, and its variability between sites and within a site (based on differences in flow), incorporation of hardness into numeric attribute states will be imperative when assessing the potential for zinc toxicity in Auckland's streams.

4.2 Possible future approaches

The best assessment of potential for toxicity is an approach that calculates different guideline values at each site for each copper and zinc measurement, based on the concentrations of TMFs at that point in time. This approach is possible when using monitoring data (e.g., SOE data). However, this approach is not feasible for model predictions, particularly given the breadth of the FWMT, as it is not realistic to measure TMF values for each modelled stream. Furthermore, as these values vary

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[5] In fact the difference may be even higher as DOC is also higher in Pakuranga Creek; however this may be moderated by the slightly higher pH in Pakuranga Creek.

over time, they would need to be measured multiple times to provide a robust indication of the site-by-site variation. A more pragmatic approach is needed, and one that is consistent with the uncertainty of the model predictions for copper and zinc.

The approach used by Healthy Waters in the AC FWMT current state assessment (Table 1-1, Chapter 1) provided a simple way to compare predictions of dissolved copper and zinc to an attribute table and to grade all the reaches modelled through the FWMT. However, two broad issues can be identified with this approach[6] based on the information presented in Chapter 3.

Firstly, categorising sites based on watershed may not be the most appropriate for the chosen TMFs as other factors are more likely to be important and have more obvious links to the known processes that affect TMFs. For example, although on average the measured water hardness across sites in the Hibiscus Coast watershed was no different to that measured in the other watersheds (excluding Wairoa and Tamaki watersheds), measured hardness at the site in Vaughan Stream (median 85 mg $CaCO_3$/L) was substantially higher than at all other sites within the Hibiscus Coast watershed (33 - 62 mg $CaCO_3$/L). Urban land cover clearly influences water hardness, with most urban sites having higher hardness (based on median) than most rural sites and all but one[7] native forest sites. Furthermore, the abundance of concrete surfaces in urban areas is known to increase hardness.

Secondly, the data used to calculate the regional average (or the catchment-based averages) may not be entirely representative of all streams and reaches in the region to which these averages are being applied. TMFs (and metals) have been measured at all streams within the SOE network since November 2017. However, the SOE monitoring data set appears to be somewhat skewed towards monitoring of urban streams: there is a higher proportion of urban streams in the monitoring network than in the entire region (31% of the monitoring network compared to <20% of the total stream network). This may result in estimates of the "average" (regional adjustment factor) TMFs being higher than they would be if measured across the entire region, because on average (based on the available data) DOC and hardness are higher in the urban streams than in those where catchment land use is dominated by native or exotic forest, or rural uses (Table 4-1).

Table 4-1: Comparison of 25th percentile and median statistics across all monitored stream sites within each land use category and overall. Units are mg/L for all data except pH. Land use categories for each stream site adopted from Ingley and Groom (2022).

Land use category	No. sites	pH		DOC		Hardness	
		25th %ile	Median	25th %ile	Median	25th %ile	Median
Native forest	6	6.9	7.1	1.2	1.8	31	32
Exotic forest	2	6.7	6.9	3.6	4.5	48	57
Rural	16	7.0	7.2	2.5	3.9	45	53
Urban	11	7.3	7.3	3.2	3.8	54	66
Overall	35	6.9	7.2	2.3	3.4	38	51

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[6] There is an additional minor issue that the guideline values should not be adjusted when hardness is less than 30 mg $CaCO_3$/L or less (see ANZG 2018), therefore the values used in the attribute table for the Wairoa watershed should be higher and equal to the default guideline values.

[7] That site (Onetangi Stream) is close to the sea and the ionic composition appears to be different to most other sites in the monitoring network, possibly due to partly saline rainwater.

Whilst the approach used in the baseline state assessment did not include any adjustment of copper guideline values for numeric attribute states, future comparisons can be expected to incorporate some form of adjustment for DOC (taking into account changes in the ANZG (2018) guideline values). The issues identified above, regarding categories used to adjust guideline values for attribute grading, and the representativeness of any data used to calculate averages are also relevant to assessing potential for toxicity from copper.

Recommendation 1

Use a more nuanced, spatially explicit method (rather than watershed-based) to adjust copper and zinc guideline values to improve the assessment of potential toxicity, due to the variation in TMFs across the region, in both space and time.

Some alternative approaches, from simplest to most complex, are to:

- categorise sites by land use,
- categorise sites by other important factors,
- categorise predictions based on flow, and
- predict TMFs at each site / time-step.

Each of these approaches are discussed in the following sections, followed by a concluding section.

4.3 Categorise sites by land use to calculate different guideline values

As described in chapter 1, the current approach used to grade FWMT predictions was to calculate different zinc guideline values based on differing hardness between watersheds. However, the analyses in chapter 3 indicate that watershed-wide relationships are a simplification of the variability in hardness (and DOC). An improved approach could be to adjust copper and zinc guideline values based on different land use in the stream catchment, given that land use is likely to be a more important driver (than watershed) of hardness and DOC. This would likely result in different thresholds for copper for streams with catchments dominated by native forest, compared to those with exotic forest, rural or urban land uses in the catchment. Similarly, different thresholds would likely apply for zinc in streams within catchments dominated by native forest and rural land use, compared to those with exotic forest or urban land use in the catchment.

However, even with a land cover based approach, there remains considerable variation in these TMFs within a land use category. For example, although hardness is typically higher (median values ≥50 mg $CaCO_3$/L) at sites where urban land use dominates the catchment, there are also sites with lower hardness. Therefore, a relatively low quantile statistic (e.g., 10th percentile) would need to be used to conservatively assess toxicity across all streams where urban land use dominates.

Recommendation 2

Use land-use categories to calculate adjustment factors (based on a low quantile statistic) to provide a closer assessment of risk from copper and zinc toxicity.

4.4 Explore additional factors for classifying sites

As discussed in sections 3.5 and 3.6, there are a wide range of factors that influence hardness and DOC in addition to the broad categories of land use. These factors may include (using hardness as an example): the total imperviousness in the catchment and directly-connected impervious surface (Tippler et al. 2014), the length of concrete-lining of the stream or of concrete-piped sections, and the specific location of sampling sites in relation to concreted reaches (i.e., within a concrete-lined reach vs 1 km downstream). If this information (or metadata) could be collected for the SOE sites, statistical analyses could be used to identify key drivers of hardness, pH and DOC, and sites could be categorised by the most important factor (or factors, using a multiple linear regression approach). These categories could then be used to calculate statistical summaries of the TMFs from available data, which could in turn be used to calculate adjusted guideline values. If that same metadata (e.g., impervious area) is available for all stream reaches, this could be used to categorise each reach modelled with the FWMT for comparison to the related set of guideline values.

Recommendation 3

Collate (or acquire) information on additional factors that may influence hardness and DOC (e.g., impervious surface, length of piping, length and/or extent of riparian vegetation) for SOE sites and undertake statistical analyses to identify key factors and generate summary statistics.

4.5 Categorise based on flow

The SOE monitoring data set indicates that high flows are associated with lower hardness at most sites, and to a lesser extent, lower pH at some sites. This suggests an approach whereby the metal predictions for each site are categorised based on flow – e.g., high flow vs baseflow – and different hardness adjustment factors are used for each category to assess the potential toxicity more accurately.

This approach would require hardness data from samples collected at high flows. An analysis of the flows during sampling (Figure 4-1) indicates there are currently gaps in the sampling of high flows at all SOE sites when compared to the flows predicted by the FWMT in the baseline state assessment. Therefore additional sampling would need to be undertaken targeting high flow events. However, high flow sampling is not easy (given that it occurs infrequently) and can be resource-intensive. One approach that could be useful for filling the gap in hardness data is to use rising-stage sampler bottles, deployed at multiple heights and a number of locations (with existing hardness and flow data). These would not be suitable for pH measurement but would be suitable for hardness.

Recommendation 4

Use rising stage samplers (or similar) to sample high flows at multiple sites to fill gaps in hardness data.

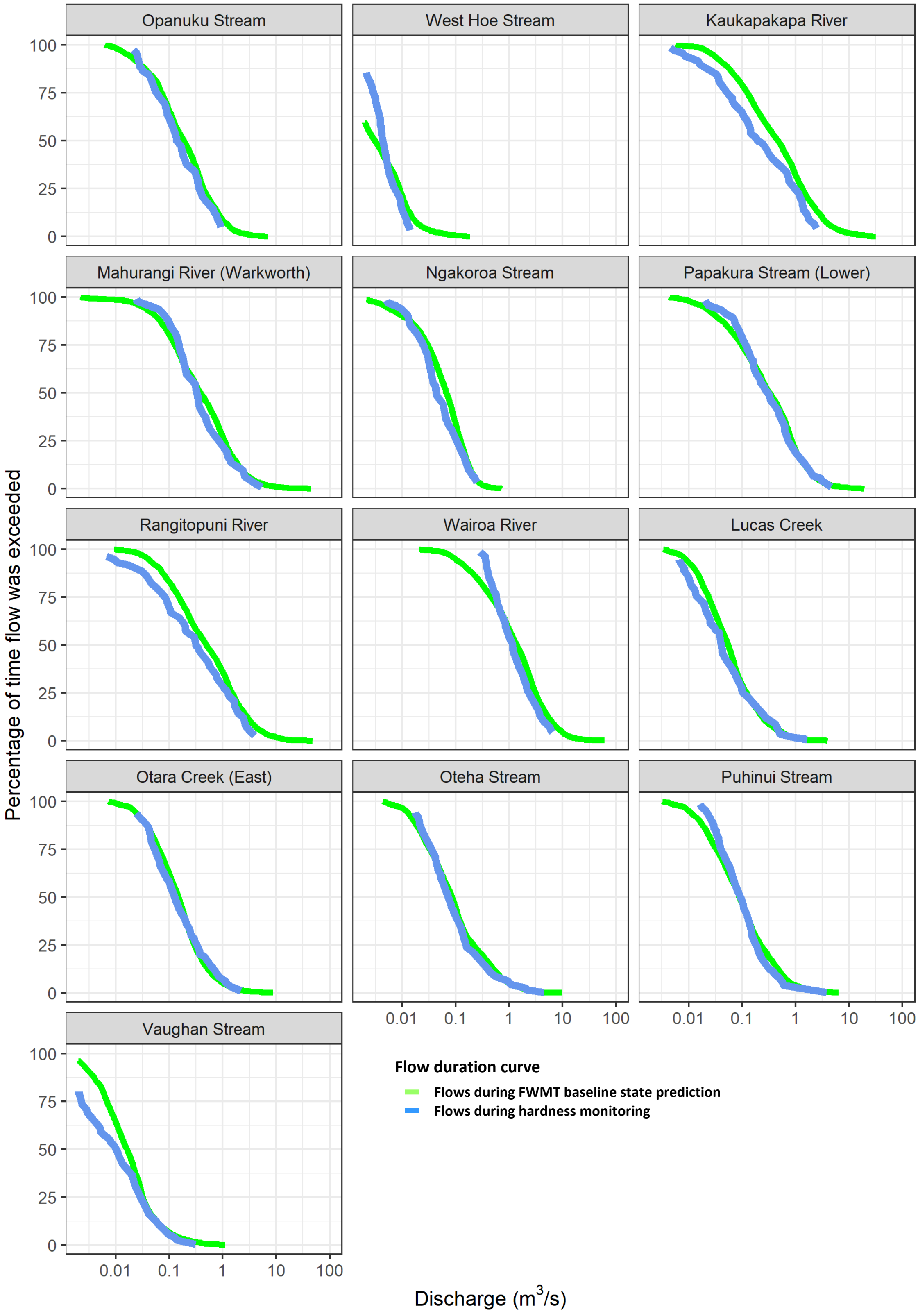

Figure 4-1: Comparison of flow duration curves from the FWMT predicted baseline state vs flow during monitoring for hardness at SOE sites. Hardness monitoring dates from November 2017 to June 2021.

4.6 Predict TMFs across the region

When assessing potential toxicity using monitoring data (e.g., SOE data), it would be possible to calculate different guideline values at each site, for every monitoring occasion. This is not feasible for FWMT model predictions, which would require predicting copper and zinc within 5,465 sub-catchments/stream reaches. In addition, it is not realistic to measure the TMF values for each stream, because these values vary over time, which may require that they are measured multiple times to provide a robust indication of the site-by-site variation.

The ideal approach would be to predict TMF values for each modelled reach and for each modelled time-step. This would require the FWMT to be supplemented with a model, either process-based or statistical, that can incorporate the key processes described in Chapter 3 of this report to predict each TMF. The TMF predictions could then be used to adjust the guideline values at each point in time for collation in attribute grading, which would provide the best estimate of potential for toxicity.

In a similar scenario in the United States, where the copper water quality guidelines use a BLM, a method was developed to predict geochemical ions at unmonitored sites. This method used correlation, categorisation by stream order and geostatistical methods (kriging) to fill the data gaps. This approach is less likely to be applicable on a regional scale in Auckland where calcium varies from around 5 to 32 mg/L between sites, compared to the United States where calcium varies from ~5 to nearly 300 mg/L. The kriging method provides for broad-scale differences but would not account for the factors such as land use, or concreting of stream beds, shown to be important at regional-scale in this assessment. Furthermore, DOC was not able to be predicted in the same way due to biases in the existing monitoring data, and instead a lower percentile (10%ile) calculated from the available data was simply recommended for use in the BLM.

It is possible that an empirical (statistical) model may be useful in predicting TMFs across Auckland streams – for example random forests or boosted regression trees, both of which use machine learning to fit the models and are widely used in stream invertebrate and water quality modelling. However, there is considerable risk in this approach. For example, there may not be sufficient TMF data to build such a model, data may not be available on key drivers of these TMFs, and some key drivers may not be known.

Recommendation 5

Explore whether it is possible to predict TMF values within the FWMT using either process-based or empirical modelling methods.

4.7 Conclusion and final recommendations

This report was commissioned by Healthy Waters (Auckland Council) for the Freshwater Management Tool programme, as part of ongoing efforts for continuous improvement in water quality accounting by Auckland Council. The report explored a range of toxicity modifying factors (TMFs) that are increasingly likely to become important in determining the potential toxicity from dissolved zinc and copper exposure in Auckland's freshwater environments. It is anticipated that these efforts will allow Healthy Waters to identify ways the outputs of the FWMT can more accurately reflect the potential effects of metal exposure on ecosystem health.

The analysis here demonstrated that variation in hardness, DOC and to a lesser extent pH, between sites and over time is of the order to meaningfully alter zinc and copper toxicity. The report finding is therefore to better capture this variation in updated versions of the numeric attribute states used in grading rivers and streams using the FWMT outputs. The specific recommendations discussed above are summarised here:

1. Refine watershed-based numeric attributes by using numeric attributes specific to land cover (e.g., urban land cover or proportion of impervious surface) which are more clearly linked to variation in temperature, pH and hardness and DOC.

2. Collate data and investigate additional factors that influence DOC and hardness, such as use of concrete for stream lining (culvert, pipe), extent of riparian vegetation, to better characterise these TMFs between sites;

3. Improve understanding of TMFs across the full hydrograph, by targeting high flow monitoring of TMFs to fill gaps in existing records – particularly for those TMFs that generally show a flow-based relationship (e.g., Ca, Mg, hardness, possibly pH); and

4. Investigate whether a model (statistical or process-based) can be developed to predict TMF concentrations, and could be applied to modelled reaches across the FWMT network to better predict metal toxicity.

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7 Glossary of abbreviations and terms

Acute toxicity	A lethal or adverse sub-lethal effect that occurs after exposure to a chemical for a short period relative to the organism's life span. Refer to Warne et al. (Warne et al. 2018) for examples of acute exposures.
Alkalinity	An indication of the buffering of water, the capacity to resist acidification, usually due to the presence of carbonates (CO_3^{2-}) and bicarbonates (HCO_3^-) in solution. This is expressed in terms of $CaCO_3$.
Anion	A negatively charged ion (having lost one or more electrons) found in solution
ANZECC	Water quality guidelines derived using the Australian and New Zealand Environment and Conservation Council risk-based methodology. The last revision of these guidelines was in 2000 and these are now superseded by the ANZG (2018) guidelines
ANZG	Australia and New Zealand Government, publishers of water quality guidelines for fresh and marine waters used in New Zealand
Attribute	Attributes are the characteristics or properties of fresh water that need to be managed for a particular value. (NPS-FM definition)
Attribute state	The level to which an attribute is to be managed. (NPS-FM definition) Each state represents a different level of water quality and is defined by a numeric range and description.
BLM	Biotic Ligand Model, a model used to account for metal bioavailability
Cation	A positively charged ion (having gained one or more electrons) found in solution
Chronic toxicity	A lethal or sub-lethal adverse effect that occurs after exposure to a chemical for a period of time that is a substantial portion of the organism's life span or an adverse effect on a sensitive early life stage. Refer to Warne et al. (2015) for examples of chronic exposures.
Cu	Copper
Dalton	A unit of mass, commonly used for small particles, proteins and polymers. It is defined as 1/12th of the mass of a carbon-12 atom
DGT	Diffusive Gradient in Thin-Film – devices that absorb selected analytes (e.g., metals) from sediment, soil or water, which can subsequently be measured.
DNPOC	Dissolved non-purgeable organic carbon – a measurement of the carbon present after the sample has been filtered then acidified and purged with purified air to remove inorganic carbon
DOC	Dissolved organic carbon – operational measurement of DOM using a carbon analyser
DOM	Dissolved organic matter – generic terminology for all forms of organic material in a filtered water sample

Fulvic acid	Large, poorly defined mixture of molecular weight organic compounds found in the environment that cannot be classified as any other chemical class of compounds (e.g., polysaccharides, proteins, etc.). Fulvic acids are derived from plant matter, soil, peat and coal and light yellow to yellow-brown in colour. They are defined as the fraction of humic substances that are soluble in water at all pH values (see humic acids below).
FWMT	Freshwater Management Tool, Auckland Council's process-based freshwater accounting and decision-making tool for water quality.
Hardness	The amount of dissolved calcium and magnesium in water, calculated as 2.5 x $[Ca^{2+}]$ + 4.2 x $[Mg^{2+}]$
Humic acid	Large, poorly defined mixture of molecular weight organic compounds found in the environment that cannot be classified as any other chemical class of compounds (e.g., polysaccharides, proteins, etc.). Humic acids are derived from plant matter, soil, peat and coal and are dark brown to black in colour. They are defined as the fraction of humic substances that is not soluble in water under acidic conditions ($pH < 2$) but is soluble at higher pH values (see fulvic acids above). They are highly aromatic and contain many carboxylic and phenolic groups.
Labile	Refers to something that can easily undergo chemical reactions, or degrade
LC50	The concentration of a substance in water or sediment that is estimated to be lethal to 50% of a group of test organisms, relative to the control response, under specified conditions. The higher the LC50, the lower the toxicity, indicating that a higher concentration was required to cause an 50% effect on the test organisms
Ligand	An ion or molecule that binds to a metal to form a complex, and generally remains in solution (i.e., dissolved, rather than precipitating)
MLR	Multiple Linear Regression
NPS-FM	National Policy Statement for Freshwater Management. New Zealand legislation which requires regional councils to establish objectives and set limits for fresh water in their regional plans.
NOF	National Objectives Framework in the NPS-FM sets out the process for regional councils and unitary authorities in setting objectives, policies and rules to manage freshwater in their regions, including setting contaminant limits.
NZ	New Zealand
Species (biological)	A group of organisms that resemble each other to a greater degree than members of other groups and that form a reproductively isolated group that will not normally breed with members of another group.
Species (chemical)	Refers to the specific form of an element in terms of its oxidation state, ionic composition, and/or complexes.
TMFs	Toxicity modifying factors – aspects of water chemistry that influence the toxicity of metals to aquatic biota

Toxicity	The inherent potential or capacity of a material to cause adverse effects in a living organism.
Toxicity test	The means by which the toxicity of a chemical or other test material is determined. A toxicity test is used to measure the degree of response produced by exposure to a concentration of chemical.
US EPA	United States Environmental Protection Agency
Zn	Zinc

Appendix A List of SOE monitoring sites and associated metadata

Table A-1: List of SOE monitoring sites for which water quality data was used in this report. Watersheds adopted from FWMT reports (Healthy Waters 2020). Dominant land use, year started and catchment area from Ingley and Groom (2022).

Watershed	Reporting name	Station number	Dominant land cover	Year pH and temp. monitoring started	DOC and hardness monitoring started	Catchment area (ha)
North East	Matakana River	6604	Rural	1986	Nov-2017	1385
Kaipara	Hoteo River	45703	Rural	1986	Nov-2017	26917
	Kaukapakapa River	45415	Rural	2009	Nov-2017	6157
	Kumeu River	45313	Rural	1993	Nov-2017	4566
	Makarau River	45505	Rural	2009	Nov-2017	4834
	Riverhead Stream	45373	Exotic	2009	Nov-2017	410
West Coast	Cascades Stream (Waitakere)	44603	Native	1986	Nov-2017	64
Mahurangi	Mahurangi River (Forestry)	6811	Exotic	1993	Nov-2017	490
	Mahurangi River (Warkworth)	6804	Rural	1993	Nov-2017	4822
Hibiscus Coast	Nukumea Stream	7171	Native	2012	Nov-2017	99
	Okura Creek	7502	Rural	2003	Nov-2017	553
	Vaughan Stream	7506	Urban	2001	Nov-2017	239
	Waiwera Stream	7104	Rural	1986	Nov-2017	3023
	West Hoe Stream	7206	Native	2002	Nov-2017	53
Waitemata	Avondale Stream	8019	Urban	2012	Nov-2017	339
	Lucas Creek	7830	Urban	1993	Nov-2017	616
	Oakley Creek	8110	Urban	1994	Nov-2017	1129
	Opanuku Stream	7904	Native	1986	Nov-2017	1566
	Oteha Stream	7811	Urban	1986	Nov-2017	1221
	Rangitopuni River	7805	Rural	1986	Nov-2017	8366
Islands	Cascades Stream (Waiheke)	74701	Rural	2013	Nov-2017	1388
	Onetangi Stream	74401	Native	2013	Nov-2017	68
Tamaki	Omaru Creek	8249	Urban	2009	Nov-2017	515
	Otara Creek (South)	8214	Urban	1985	Nov-2017	880
	Otara Creek (East)	8205	Urban	1992	Nov-2017	1828
	Botany Creek	8217	Urban	1992	Nov-2017	665
	Pakuranga Creek	8215	Urban	1992	Nov-2017	216
Manukau Harbour	Ngakoroa Stream	43829	Rural	1993	Nov-2017	466
	Papakura Stream (Upper)	1043837	Rural	2012	Nov-2017	2324
	Papakura Stream (Lower)	43856	Rural	1993	Nov-2017	4716
	Puhinui Stream	43807	Urban	1994	Nov-2017	1304
	Waitangi Stream	43601	Rural	2009	Nov-2017	1897
	Whangamaire Stream	438100	Rural	2009	Nov-2017	814
Wairoa	Wairoa River	8516	Rural	1986	Nov-2017	14855
	Wairoa Tributary	8568	Native	2009	Nov-2017	227